PROCEEDINGS

OF THE

INDIAN ACADEMY OF SCIENCES

VOL. XXII

SECTION A

CONTENTS

SECTION A—VOL. XXII

No. 1—July, 1945

PAGE

PAGE

iv

CORRECTION

Vol 22, No. 2, Sec A, August 1945

n the article entitled "The Azimuthal Effect of Cosmic Rays at Lahore" by P. S. Gill.—

ptions of the two figures have been interchanged **Fig. 2** should be **Fig. 1**, Fig. 1 should be **Fig. 2** and then the captions given would read correct."

CORRECTION

Vol. 22, No. 2, Sec. A, August 1945

In Plate I, facing page 66, in the first line *interchange* the words "2nd Positive" "1st Positive".

THE THEORY OF HOMOMORPHISMS AND CONGRUENCES FOR PARTIALLY ORDERED SETS*

By V. S. Krishnan, M.A., M.Sc.

INTRODUCTION

In the study of the abstract structures of General Algebra, the concepts of the Homomorphism and the Congruence play a fundamental role. We begin with some preliminary definitions and results relating to these concepts† when considered for general structures.

A *homomorphism* from one (algebraic) *structure* K to a second similar structure K′ is a mapping, f, of K on K′ which carries over the fundamental structural features of K into the corresponding features of K′. Thus the map f is a *homomorphism from K to K′ relative to an operation, $θ$,*—[or *relative to a binary relation R]*—if $c = θ \{c_i\}$ in K implies $f(c) = θ \{f(c_i)\}$ in K′;—[if $c R d$ in K implies $f(c) R f(d)$ in K′] A homomorphism with a unique inverse which is also a homomorphism is an *isomorphism*. Isomorphic structures are identical in their formal features.

Now given any map, f, of one *set* K on another *set* K′, we can define an *associated equivalence relation*—[i.e., a reflexive, symmetric and transitive relation]—$E = E(f)$ by the condition: xEy holds for x, y in K if, and only if, $f(x) = f(y)$ in K′. Conversely to any given equivalence relation E on K we can find a map, f, of K on another set such that $E =$ the equivalence $E(f)$ associated with this map, f. For if we denote by $e(x)$ the subset of those elements y of K satisfying xEy, then any two of these subsets are either coincident or disjoint. Hence there is a mapping e of the elements of K on these subsets $e(x)$, so that if we denote by " K/E " the family of distinct " cosets " of the form $e(x)$, e is a mapping of K on K/E for which $E(e) = E$. We call K/E the "*quotient of K by the equivalence E*" (by analogy with similar quotient structures in Modern Algebra). This map e of K on K/E is, in a sense, typical of all those maps f of K on other sets

---

for which E is the associated equivalence. For if $E(f) = f$, there is a one-to-one reversible correspondence $e(x) \rightleftarrows f(x)$ between the elements of K/E and those of $K' = f(K)$, which enables us to pass from either set to the other by a mere re-naming of the elements. And under these passages the maps e and f go over one into the other. Therefore these two maps cannot differ in any of their formal features.

So much for mappings of one *set* on another. If we now consider mappings of one (algebraic) *structure* K on another K' of the same type, the equivalences associated with the special types of maps, "the homomorphisms", will be of special nature. We call such equivalences " *homomorphic equivalences* " or " *h-equivalences* " (relative to θ or R), if the map is a homomorphism relative to θ or R). These *h*-equivalences may be characterised in the following manner:

> (I, 1) *for a given equivalence relation, E, on K to be a* h-*equivalence*— *(relative to θ or R)—it is necessary and sufficient that it should be possible to give to the set K/E a structure of the same nature as that of K in such a way that the map* e *of K on K/E becomes a homomorphism (relative to θ or R).*

The condition is evidently sufficient; for when K/E has a structure similar to K and e is a homomorphism from K to K/E then, since $E(e) = E$, E must be a *h*-equivalence. Conversely if $E, = E(f)$, is the equivalence defined by a homomorphism from K to a similar structure K', $= f(K)$, then using the reversible correspondence $e(x) \rightleftarrows f(x)$ between K/E and K', the structure of K' can be transferred to K/E, and then e would become a homomorphism, since f is such a homomorphism and e, f must be of the same formal nature.

We now introduce the notion of the *congruence relative to an operation.* An equivalence relation, E, on K is a " *congruence relative to an operation θ,*" if the *cosets,* $e(x)$, of K relative to E, combine by the elementwise operation θ: that is $e(\theta\{c_i\})$, $e(\theta\{d_i\})$ are identical for any family $\{(c_i, d_i)\}$ of pairs, (c_i, d_i), of equivalent elements. Or, in other words,

> (I, 2) *an equivalence relation E on K is a congruence relative to θ if, and only if,* $\theta\{c_i\} E \theta\{d_i\}$ *is true whenever* $\theta\{c_i\}$, $\theta\{d_i\}$ *exist in* K^1, *and each of the pairs* (c_i, d_i) *satisfies* $c_i E d_i$.

Since the cosets combine by the elementwise operation θ, we can define an operation, θ^*, on the family K/E, of these cosets by writing $x = \theta^*\{x_i\}$ if, and only if, $\theta\{c_i\}$ exists in K and lies in the coset x for some choice of elements, c_i, one from each x_i. [As E is a congruence relative to θ,

---

[1] We do not assume here that K is closed for the operations θ.

x is independent of the choice of the c_i's from the v_i's.] We shall call *θ^* the associated operation* on the quotient, K/E, of K by the congruence E relative to θ.

The significance of the *congruence* notion in the study of homomorphisms arises from the fact that:

(I, 3) every *h*-equivalence on K relative to an *operation*, θ, is a congruence relative to θ

For if $E = E(f)$ is the *h*-equivalence associated with a homomorphism f relative to θ from K to K', $= f(K)$, the existence of θ {c_i} and θ {d_i} in K implies the existence of θ {$f(c_i)$} $= f(\theta \{c_i\})$ and θ {$f(d_i)$} $= f(\theta \{d_i\})$ in K' while $c_i E d_i$ for each (c_i, d_i) implies $f(c_i) = f(d_i)$ for each (c_i, d_i), and so $\theta \{f(c_i)\} = \theta \{f(d_i)\}$. Hence $f(\theta_i\{c_i\}) = f(\theta_i\{d_i\})$, and so $\theta \{c_i\}$ E $\theta \{d_i\}$ is true.

With these preliminary remarks we pass on to the subject proper, namely the study of homomorphisms and *h*-equivalences for a special class of algebraic structures, "the partially ordered sets."

1. THE *h*-CONGRUENCES ON PARTIALLY ORDERED SETS[2]

Since the ordering relation is a fundamental structural feature of a partially ordered set, homomorphisms between partially ordered sets will be understood to be, in the first instance, homomorphisms relative to the ordering relation. A homomorphism may also be relative to any selection of order-operations [*i e*, operations that may be defined in any partially ordered set solely in terms of the ordering relation] Since the *h*-equivalence associated with such a homomorphism relative to an order-operation, θ, must also be a congruence relative to θ—by (I, 3)—, we shall call such *h*-equivalences "*h*-congruences" relative to θ

From the condition (I, 1) established earlier for an equivalence to be a *h*-equivalence, it now follows that

(1, 1) *for an equivalence relation, E, on a partially-ordered set K to be a* h*-congruence relative to an (order) operation* θ, *it is necessary and sufficient that it should be possible to give to the set K/E an order-structure such that e becomes a homomorphism from K to K/E relative to* θ *(and also the ordering relation)*

Or, in other words,

(1, 2) E *is a* h*-congruence on K if, and only if, an ordering relation* $<^*$ *can be found for K/E such that*. (a) $x < y$ *in* K *implies*

e (x) <* e (y) *in* K/E, and (b) x = θ {x_i} *in* K *implies* e (x) = θ {e (x_i)} *in* K/E, *the operation* θ *for* K/E *being defined in terms of* <* (*in the same way as* θ *is defined in* K).

In the above, the condition (b) not only implies that E should be a congruence relative to θ, but even more. It is, in fact, equivalent to the following two conditions [as may be easily verified]:

        (b_1) E *is a congruence relative to* θ, *and* (b_2) *if* θ* *is the associated operation defined on* K/E, *and* θ *the order-operation on* K/E *defined in terms of* <*, *then* x = θ* {x_i} *implies* x = θ {x_i}.

So, summing up, the necessary and sufficient conditions for an equivalence E on K to be a *h*-congruence relative to θ are.

    (1, 3) (A): E *is a congruence relative to* θ; *and there is an ordering relation* <* *on* K/E *satisfying the conditions* ·

        (B): x < y *in* K *implies* e (x) <* e (y) *in* K/E; *and*

        (C): x = θ* {x_i} *implies* x = θ {x_i}. [θ* *being defined when* E *is a congruence relative to* θ, *and* θ *being defined for* K/E *in terms of* <*].

Among these conditions only (B) and (C) involve the ordering relation <* which is to be found for K/E. Also (C) implies (B), since θ* is uniquely defined only when E is a congruence relative to θ. Hence, regarding the mutual dependence of these three conditions, we have yet to consider the following questions:

    (1) Does (B) imply (A)?

    (2) Do (A) and (B) imply (C), either individually or jointly?

    (3) Do (C) and (A) imply (B), either individually or jointly?

    (4) Can (A), (B) and (C) hold good for more than one ordering relation on K/E? In other words, can K/E have more than one distinct order-structure such that *e* is a homomorphism?

These questions we now answer by considering some examples.

Note.—The Figs. I to IV are the Hasse Diagrams[3] for the ordered sets considered in the four examples, and these give the order-structures of the ordered sets in each case. The nature of the equivalence E is specified, in each case, by giving the partition of K into the cosets, e (x), which form the elements of K/E.

Example 1. Let θ denote finite addition, and E = (0), (*a*, *b*), (1) for the additive system illustrated in Fig I. E is not a congruence relative to θ, as *a* = *a* + *a* and 1 = *a* + *b* are not equivalent, though *a* and *b* are

equivalent.   There is an ordering relation on K/E satisfying condition (B), namely the reflexive, transitive relation $<^*$, which satisfies further the conditions: $(0) <^* (a, b)$, $(a, b) <^* (1)$.   Hence (B) *does not imply* (A)

   Example 2.   Let θ denote finite addition, and E $= (a_1, b_1, c_1)$, (a_2, a_3), (b_2, b_3), (c_3, c_3) for the ordered set illustrated in Fig. II.   E is a congruence relative to θ [since the only sums with distinct summands are $a_1 = a_1 + a_2$, $b_1 = b_1 + b_2$, $c_2 = c_1 + c_2$, $c_3 = a_3 + c_3$, $c_2 = b_3 + c_3$, and $c_3 = a_3 + b_3$]   There is one, (and only one), ordering relation on K/E for which condition (B) is true; namely the reflexive, transitive relation $<^*$ on K/E satisfying $(a_2, a_3) <^* (a_1, b_1, c_1)$, $(b_2, b_3) <^* (a_1, b_1, c_1)$, and $(a_1, b_1, c_1) <^* (c_2, c_3)$ But for this ordering relation on K/E the condition (C) is not true, as $a_3 + b_3 = c_3$, but $e(a_3) + e(b_3) = e(c_1) + e(c_3)$ Hence (A) and (B) *do not imply* (C) *jointly, and so cannot imply* (C) *individually either.*
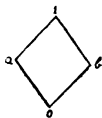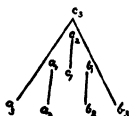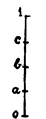
FIG. I   FIG. II   FIG III   FIG. IV

   Example 3.   Let θ denote product-complementation in K, and let E $= (0)$, (a, c), $(b, 1)$ for the "chain" illustrated in Figure III   Then E is a congruence relative to θ, since $a' = c' = 0$, $b' = 1' = 0$.   There is an ordering relation on K/E for which condition (C) is true, namely the reflexive, transitive relation $<^*$ satisfying. $(0) <^* (a, c)$, $(a, c) <^* (b, 1)$ For under this ordering relation, $(0)' = (b, 1)$ and $(a, c)' = (b, 1)' = (0)$, so that $0' = 1$, $a' = b' = c' = 1' = 0$ imply $e(0)' = e(1)$, and $e(a)' = e(b)' = e(c)' = e(1)' = e(0)$.   But for no ordering relation on K/E can condition (B) be true, as $a < b$, $b < c$ would imply $e(a) <^* e(b)$, $e(b) <^* e(c)$, and as $e(a) = e(c)$, it would lead to $e(b) = e(c)$, which is false.   Hence (A) and (C) *do not imply* (B) *jointly, and so cannot imply* (B) *individually either.*

   Example 4.   Let θ denote finite addition, and E $= (a)$, (b), (c), (d) for the ordered set K illustrated in Fig IV   Then there are two ordering

---
   * In the diagram an element a is $<$ another b if there is a *chain* of constantly ascending segments going from a to b.   For a description of Hasse Diagrams see Birkhoff's "Lattice Theory".

relations on K/E for which all three conditions (A), (B) and (C) are true; namely the reflexive, transitive relations $<^*$, $<'$ satisfying the conditions: $(a) <^* (b)$, $(b) <^* (c)$, $(d) <^* (c)$, and $(a) <' (c)$, $(d) <' (c)$, $(e) <' (b)$. Hence *the conditions (A), (B) and (C) may hold for more than one distinct ordering relation on K/E.*

2. HOMOMORPHISMS AND h-CONGRUENCES AMONG ADDITIVE SYSTEMS, MULTIPLICATIVE SYSTEMS AND LATTICES*

The principal result in the congruence theory for additive systems is:

(2, 1) every congruence relative to finite addition on an additive system is a h-congruence relative to finite addition, so that congruences and h-congruences now coincide.

For when E is a congruence relative to finite addition on an additive system K, since K is closed for the binary operation '+' which is commutative, associative and tautological, it is readily verified that K/E is closed for the associated operation $+^*$, and that this operation is also commutative, associative and tautological. Thence it follows[4] that K/E is an additive system with $+^*$ denoting addition, the ordering relation $<^*$ being defined by the condition. $e(x) <^* e(y)$ if, and only if, $e(x) +^* e(y) = e(y)$ [or $e(x+y) = e(y)$]. And e is a homomorphism from K to K/E relative to finite addition for which the associated h-congruence is E itself Hence E is a h-congruence relative to finite addition.

We saw, (by Example 4), that K/E may have distinct order-structures under which e is a homomorphism from K to K/E relative to θ But we can now show that:

(2, 2) there is only one order-structure for K/E under which e is a homomorphism relative to finite addition from K to K/E; this order-structure is that described above, when the associated operation $+^*$ is taken as the addition-operation for K/E.

For if e is such a homomorphism, when K/E is ordered by an ordering relation $<'$, then condition (C) of (1, 4) must be true for K/E ordered by $<'$. Hence as K/E is closed for $+$, $x+'y$ exists for every pair of elements x, y of K/E, and equals $x+^*y$. As $x<'y$ is equivalent to $x+'y=y$ and $x<^*y$ is equivalent to $x+^*y=y$, it follows that $x<'y$ if, and only if,

---

* An *additive system* contains the sum, $a+b$, of any two of its elements a, b; a *multiplicative system* contains the product, $a\,b$, and a *lattice* both the sum and product, an additive system can be characterised as a set closed for a binary operation $+$ which is commutative $-(x+y=y+x)$, associative $-(x+y+z=x+y+z)$, and tautological $-(x+x=x)$, with the ordering relation, $<$, related to $+$ by $x<y$ if, and only if, $x+y=y$.

$x <^* y$. So the ordering relation $<^*$ is the only one for K/E under which e is a homomorphism relative to finite addition from K to K/E. So we may now, without ambiguity, talk of ' *the homomorph K/E* ', or the ordered set K/E, meaning thereby the set K/E ordered by the relation $<^*$ defined as above.

We now consider how, in a natural manner, a finite succession of additive homomorphisms between consecutive pairs of a family of additive systems K, K', K'', . . may be combined into one and how a single additive homomorphism can be resolved into such a succession of homomorphisms.

> (2, 3) *if* g *and* h *are additive homomorphisms from* K *to* K' *and from* K' *to* K'' *respectively, there is an additive homomorphism* f — h . g—*the* ' *product* ' *of* g *and* h—*from* K *to* K''; f (x), *for any* x *in* K, *is defined to be equal to* h [g (x)]

> (2, 4) *if* g *and* f *are additive homomorphisms from* K *to* K' *and from* K' *to* K'' *respectively, and if* g (x) = g (y) *implies* f (x) = f (y) *(for* x, y∈K), *then* f *can be resolved into factors* g *and* h, *so that* f = h . g, *where* h *is an additive homomorphism from* K' *to* K''; h (x'), *for any* x', = g (x) — x∈K, *of* K', *is defined to be equal to* f (x).

The proofs of these results follow immediately from the definition of the additive homomorphism.[5]

Note.—Before concluding this section, we may observe that there is a natural order-structure for the family of equivalence relations on a set K, and hence, also, for the sub-family of *additive congruences*—or congruences relative to finite addition—on K, when K is an additive system.

> The equivalence relations on a set K form a complete lattice $E (K)$; and when K is an additive system, the additive congruences on K form a complete lattice, $K (+)$, contained in $E (K)$ and with the same operations of addition and multiplication as $E (K)$.[6]

---

[5] These may also be deduced from a general theorem (Theorem 4), regarding the isomorphism of a quotient structure and the quotient structure of a quotient structure, proved in my paper "On binary relations, "

[6] The structure of the lattices E (K), K (0)—where θ is an operation of finite index, for which K is closed—has been considered in the paper "On binary relations " In E (K) the sum $E_1 + E_2$ of two equivalences satisfies the conditions · $x (E_1 + E_2) y$ if, and only if, any consecutive pair $(x_{i-1}, x_i)-i = 1, \ldots n$, of elements of a certain sequence $x_0, \ldots, x_n$ of elements of K are equivalent under E_1 or E_2, and $x_0 = x$, $x_n = y$.

The analogues of all results in this section can be proved, by similar methods, *for multiplicative congruences and homomorphisms* among multiplicative systems, and *for lattice congruences and homomorphisms (i.e.,* congruences and homomorphisms relative to finite addition and multiplication) among lattices.

3   REGULAR AND IRREDUCIBLE ADDITIVE CONGRUENCES AND HOMOMORPHISMS AMONG ADDITIVE SYSTEMS WITH ZEROS

When K is an additive system with a zero, 0, to each additive congruence E on K can be associated a μ-ideal[7] of K, namely the subset $e(0)$ of elements congruent to 0 [For aE0, bE0 imply $(a+b)$ E $(0+0)$ or $(a+b)$ E0, and aE0, $c \div a$ imply $(a+c)$ E $(0+c)$ or aEc and aE0, whence cE0 follows] Given any μ-ideal C of K there exist additive congruences E for which the associated ideal $e(0) =$ C, since the congruence, $\bar{C}$, modulo the μ-ideal C,[8] defined as under, is such a congruence; $\bar{C}$ is defined by:

> (3, 1) $x\bar{C}y$—*or* x ≡ y (mod C)—*if, and only if,* x + z = y + z, *for some element z from* C.

That $x \equiv 0$ (mod C) is equivalent to $x \epsilon$C is easily verified   The congruence $\bar{C}$ can be characterised as the least among all congruences, E, with $e(0) =$ C. For $x \equiv y$ (mod C) or x + z = y + z and zE0 imply $(x + z)$ E x, $(y + z)$ Ey, and so xEy [as E is an equivalence relation].   These minimals among additive congruences, under which the same subset of elements are congruent to 0, we shall call ' *the regular additive congruences* '.   The regular congruences are, thus, the same as the congruences modulo the μ-ideals of K   We shall denote the quotient additive system, K/$\bar{C}$, of K by the regular congruence $\bar{C}$ also by K/C; the elements of K/C, *i.e.*, the

---

[7] Ideals in Boolean rings and distributive lattices have been studied in detail by M H Stone (in his papers on " The Theory of Representations for Boolean Algebra " and on " Topological Representations of Distributive lattices . ")   For any additive system K, the μ-ideals form a *complete* lattice K$_{\mu}$—$l \epsilon$, a lattice containing the sum and product of every sub-family of its elements , the product of ideals is given by their set intersection, and the sum by the μ-ideal generated from their set-union   The μ-ideal Ā generated from any subset A being defined as the set of elements of K which are < the sums of finite subsets of A   When A is a one-element subset, (a), the ideal Ā is called a ' Principal μ-ideal ' and is denoted by P$_{\mu}$ (a)   Evidently P$_{\mu}$ (a)+P$_{\mu}$ (b) = P$_{\mu}$ (a+b) and P$_{\mu}$ (a)·P$_{\mu}$ (b) = P$_{\mu}$ (a·b), if a·b exists in K   Dual results are true for α-ideals of a multiplicative system ; and all these are true of a lattice

[8] In a Boolean ring, which has a lattice structure as well as a ring-structure, the μ-ideals and ring-ideals coincide and the congruences modulo these ideals also get identified (*cf.* Stone's " Theory of Representations . ", Th. 44).

cosets $e(x)$ of K modulo $\bar{C}$, are called "*the residue-classes of K modulo C*". The ideal C itself is one residue-class, namely the one containing 0.

As a subset of the lattice K (+), the family $\overline{K(+)}$ of the regular additive congruences has an order-structure; this may be characterised in the following manner:

(3, 2) the family $\overline{K(+)}$ of regular additive congruences on K forms a complete lattice isomorphic to the lattice, K_μ, of all μ-ideals of K; the addition in $\overline{K(+)}$ is the same as in K (+).

The isomorphism follows from the fact that $C \to \bar{C}$ is a reversible one-to-one correspondence between the elements of K_μ and those of $\overline{K(+)}$, and if $C \to \bar{C}$, $D \to \bar{D}$, then $C \subset D$ implies and is implied by $\bar{C} < \bar{D}$. From the nature of the lattice structures of K (+) and K_μ, the sum in K (+) of any family of elements of $\overline{K(+)}$ can be shown to be in K (+), so that it must be the sum of the elements in K (+) also.

The additive congruences, E, for which the ideal $e(0)$ of elements congruent to 0 reduces to the single element set (0), $= P_\mu(0)$ form, in a sense, a complementary type of congruence to the regular ones. We call these "*the irreducible additive congruences*" The only regular and irreducible congruence is the identity relation I, connecting only the pairs of identical elements of K [as $x \equiv y \pmod{P_\mu(0)}$ implies $x + 0 = y + 0$ or $x = y$].

We now define an *additive homomorphism*, f, from an additive system K with zero, 0, to another K' [with $f(0)$ as zero], to be '*regular*' or '*irreducible*' according as the associated additive congruence $E_f = E(f)$, on K is regular or irreducible The only regular and irreducible homomorphism is the identity relation I, and so $f(x) = f(y)$ if, and only if, $x = y$; and $x < y$ or $x + y = y$ if, and only if, $f(x) + f(y) = f(y)$ or $f(x) < f(y)$].

We now show how any additive homomorphism has a certain fundamental and unique resolution into a regular part and an irreducible part.

THEOREM 1. *Any additive homomorphism,* f, *from one additive system* K, *with zero, to another* K', *can be resolved uniquely into the product of a regular additive homomorphism* g *from* K *to another additive system* K", *and an irreducible additive homomorphism* h *from* K" *to* K'; *so that* $f = h \cdot g$.

Proof.—If E is the additive congruence $E(f)$ on K associated with f, and C = the ideal $e(0)$, then $\bar{C} \subset E$, as $\bar{C}$ is the minimal congruence under which C is the ideal of elements congruent to 0. Hence if we take K" = K/C,

10 V. S. Krishnan

and let g denote the regular additive homomorphism from K to K/C, [under which $g(x)$, for any x in K, is the residue-class modulo C containing x], then $g(x) = g(y)$ implies $f(x) = f(y)$. Therefore, by (2, 4), f can be resolved in the form $f = h \cdot g$, where g is the regular additive homomorphism from K to K/C and h is an additive homomorphism from K/C to K'. We can show that h is irreducible; for if $h(x) = 0' = f(0) =$ the zero of K' for some element X [$= g(x) = x\epsilon K$] of K/C, then $f(x) = h[g(x)] = h(X) = 0' = f(0)$, and so $x\epsilon 0$ follows. Hence $x\epsilon C$ and $x = 0 \pmod{c}$ or $X = g(x) = C =$ the zero of K/C. So h is irreducible

This resolution is unique; for if $f = h' \cdot g'$ is another resolution into a regular part g' and an irreducible part h', then the regular congruence on K associated with g and with g' must be the same. For otherwise E (g') must be the congruence modulo a μ-ideal D + C. This D must be ⊂ C, as $d\epsilon D$ implies, in succession, $d = 0 \pmod{D}$, $g'(d) = g'(0)$, $f(d) = h' [g'(d)] = h' [g'(0)] = f(0) =$ the zero of K, and so $d\epsilon C$. But if D ⊂ C, and D + C, then there is a c in C which is not in D, so that $f(c) = h[g(c)] = h[g(0)]$ $f(0)$ or $h'[g'(c)] = f(c) = f(0) = h'[g'(0)]$, though $g'(c) + g'(0) =$ the zero of $g'(K)$, as $g'(c) - g'(0)$ would imply $c = 0 \pmod{D}$ or $c\epsilon D$ Thus D ⊂ C and D + C imply that h' is not irreducible. So, since h' is irreducible, C ⊃ D and C̄ ⊃ D̄ So g' and g, to which the same congruence C̄, D̄, on K is associated, can differ only by an isomorphism factor; thence, it also follows that, h and h' can only differ by an isomorphism factor (as $h \cdot g = h' \cdot g'$). So neglecting isomorphism factors $h \cdot g$ is a unique resolution of f

As immediate deductions from the theorem, we have the corollaries.

Corollary 1.—The homomorphism f is regular if, and only if, the factor h is an isomorphism

Corollary 2.—The homomorphism f is irreducible if, and only if, the factor g is an isomorphism

We now consider how the regular and irreducible homomorphisms combine or resolve by themselves

(3, 3) *The product of two successive regular additive homomorphisms is also regular additive, and the product of two successive irreducible additive homomorphisms is also irreducible additive.*

(3, 4) *The last factor, (g_n), in any resolution, $(g_n \cdots g_1)$, of a regular additive homomorphism is regular; and every factor in any resolution of an irreducible additive homomorphism is irreducible.*

Note.—An example of a regular additive homomorphism is the following: If *a* is any fixed element of an additive system **K**, and we define $f(x) = a + x$, for each *x* of **K**, then *f* is a regular additive homomorphism from **K** to the additive sub-system $P_a(a)$ (of elements of **K** which are $> a$).

Duals of all the results of this section can be proved by exactly similar methods for multiplicative systems with ones. [Any regular multiplicative congruence would be the congruence, $\tilde{D}$, modulo an *o*-ideal **D** defined by: $x\tilde{D}y$ or $x \equiv y \pmod{D}$ if, and only if, $x \cdot z = y \cdot z$ for some *z* from **D**.]

4. REGULAR AND IRREDUCIBLE LATTICE CONGRUENCES AND HOMOMORPHISMS AMONG LATTICES WITH UNITS

We now proceed to define regularity and irreducibility for lattice congruences among lattices with units

Since, in the lattice, the operations of addition and multiplication occur symmetrically, and μ- and *o*-ideals also enter on the same footing, we first define a lattice congruence in terms of a pair of ideals—a μ-ideal **C** and an *o*-ideal **D**—of the lattice, **K**, with units. It is known that the lattice congruences on **K** form a complete lattice, **K** $(+, \cdot)$, contained in the lattice, **E** (**K**), of all equivalences on **K** and having the same addition and multiplication.[9] So the lattice product in **E** (**K**) of all the lattice congruences which are $\supset \bar{C}$ and $\supset \tilde{D}$ is a lattice congruence, and the least one $\supset \bar{C}, \supset \tilde{D}$ [and so the least one $\supset \bar{C} + \tilde{D} =$ the sum in **E** (**K**) of $\bar{C} + \tilde{D}$] We denote this lattice congruence by $(\bar{C}, \tilde{D})$, and call it *the lattice congruence modulo the pair of ideals* (*C*, *D*).

If **E** is any lattice congruence on **K** and $\bar{C} - e$ (0), $D = e$ (1) then, since $\bar{C} \subseteq$ **E** and $\tilde{D} \subseteq$ **E**, $(\bar{C}, \tilde{D}) \subseteq$ **E** also So $(\bar{C}, \tilde{D})$ is the least of the lattice congruences, E_i, on **K** for which e_i (0) = **C** and e_i (1) = **D**.[10] We call these minimal lattice congruences "*regular lattice congruences*" So a regular lattice congruence, **E** is the congruence modulo a pair of ideals [namely *e* (0) and *e* (1)] Conversely also, any lattice congruence, **E** = $(\bar{C}, \tilde{D})$, modulo a pair of ideals (*C*, *D*) of **K**, is regular For if P = *e* (0) and

---

[9] This result is analogous to the one given for additive congruences in the Note at the end of § 2, and is a special case of a general result proved in my paper "On Binary Relations, Congruence and Homomorphisms," and also in Birkhoff's paper "*On the structure of Abstract Algebras*"

[10] $(\bar{C}, \tilde{D})$ is one such congruence E_i, for *c*∈C and *d*∈D imply *c*$\bar{C}$0, *d*$\tilde{D}$1 and so *c* $(\bar{C}, \tilde{D})$ 0, *d* $(\bar{C}, \tilde{D})$ 1 ; while *c* $(\bar{C}, \tilde{D})$ 0, *d* $(\bar{C}, \tilde{D})$ 1 imply *c*E0, *d*E1 and so *c*∈C, *d*∈D As $(\bar{C}, \tilde{D}) \subseteq$ **E**, if *e* (0) = **C** and *e* (1) = **D**, it follows that $(\bar{C}, \tilde{D})$ is the least of such lattice congruences, **E**.

$Q = e(1)$, as before $(\bar{P}, \bar{Q}) \in E$; while $x \epsilon C$, $y \epsilon D$ imply $x\bar{C}0$, $y\bar{D}1$ and so $x (\bar{C}, \bar{D}) 0$, $y (\bar{C}, \bar{D}) 1$ or $x E0$, $y E1$ are true, whence follow $x \epsilon P$ and $y \epsilon Q$. Hence $C \subset P$ and $D \subset Q$, so that $E = (\bar{C}, \bar{D}) \subset (\bar{P}, \bar{Q})$ [since $(\bar{P}, \bar{Q})$ being a lattice congruence $\supset \bar{P} \supset \bar{C}$ and $\backsim \bar{Q} \supset \bar{D}$, it must be $\supset$ the least lattice congruence $(\bar{C}, \bar{D})$ which is $\supset \bar{C}$ and $\supset \bar{D}$)]. Hence $E = (\bar{P}, \bar{Q})$ where $P = e(0)$ and $Q = e(1)$; that is, E is regular. In general $C \vdash P$ and $D \ast Q$; evidently the pair (P, Q) could be characterised as the maximal among the pairs (C, D) for which $E = (\bar{C}, \bar{D})$. We call this pair *the canonical pair* defining the regular congruence E, and call $(\bar{P}, \bar{Q})$ the *canonical form* of E. Evidently if $(\bar{P}_1, \bar{Q}_1)$ and $(\bar{P}_2, \bar{Q}_2)$ are in canonical form then $(\bar{P}_1, \bar{Q}_1) \subset (\bar{P}_2, \bar{Q}_2)$ if, and only if, $P_1 \subset P_2$ and $Q_1 \subset Q_2$.

We next define *a lattice congruence E* on the lattice K *to be irreducible* if $e(0) = (0) = P_\mu(0)$ and $e(1) = (1) = P_\alpha(1)$. The only regular and irreducible lattice congruence is the identity relation I on K [since $x = y$ [mod $P_\mu(0)$] and $x = y$ [mod $P_\alpha(1)$] each imply $x = y$]

Corresponding to these two types of congruences, we define *a lattice homomorphism, f,* form a lattice K with units, 0, 1, to another K' [with units $f(0)$, $f(1)$], *to be regular or irreducible* according as the lattice congruence, $E(f)$, associated with f is regular or irreducible.

We can prove, by almost the same methods, a resolution theorem for lattice homomorphisms analogous to Theorem 1, and also the analogues of the results (3, 3) and (3, 4) for regular and irreducible lattice homomorphisms.

Examples of regular lattice homomorphisms are the maps g and h from a distributive lattice[11] K to the sub-lattices K', K'' consisting respectively of the elements of K lying between a and $a + b$, and of elements of K lying between $a . b$ and a; where a, b are fixed elements of K, and $g(x) = a + b . x$ and $h(x) = a . (b + x)$, for any x of K.

Among regular lattice homomorphisms there are some of special interest. Thus if (C, D) is a pair of ideals of a lattice K such that $\bar{C}$ and $\bar{D}$ are both *lattice* congruences, then $(\bar{C}, \bar{D}) = \bar{C} + \bar{D}$; and any lattice homomorphism, f, of K on a lattice K' for which the associated congruence $E(f)$

---

[11] A lattice is *modular* if, for any elements a, b, c, $a > b$ implies $a . (b + c) = b + a . c$; it is *distributive* if, for any a, b, c, $a . (b + c) = a . b + a . c$. These laws imply also their duals.

A lattice is *complemented* if to each element, a, there is a *complement*, b, such that $a + b = 1$ and $a . b = 0$.

on K is $(\bar{C}, \bar{D})$ can be resolved into two lattice homomorphisms g, h of which one is a regular additive, and the other a regular multiplicative homomorphism. [For instance g may be taken to be the regular additive homomorphism from K to K/C, where $g(x)$, for any x of K, is defined to be the residue-class modulo C containing x; g is a lattice homomorphism, as $\bar{C}$ is a lattice congruence, and as $g(x) = g(y)$ implies $f(x) = f(y)$, there is a lattice homomorphism, h, from K/C to K' such that $f = h\,g$; from the fact that $E(f) = \bar{C} + \bar{D}$, it could be deduced that h is regular multiplicative] Hence those ideals of a lattice modulo the congruence which are *lattice* congruences are of special interest. Such ideals can be completely characterised as follows:

THEOREM 2   *The congruence modulo a μ-, [or a-], ideal C of K is a lattice congruence if, and only if, C is distributed by all finite lattice products in the lattice, K_μ [in K_a], of all μ-, [a-], ideals of K.*

Proof.—If C is a μ-ideal of K such that $\bar{C}$ is a lattice congruence, then C is distributed by all finite products in K_μ; that is $C + D.E = (C+D).(C+E)$, for any D, E from K_μ

For $C + D E \subseteq (C+D)$ and $\subseteq (C+E)$, and so $\subseteq (C+D)\cdot(C+E)$. On the other hand if $x \epsilon (C+D).(C+E)$, $x \epsilon (C+D)$ and $x \epsilon (C+E)$, so that elements c, c' from C and d, e from D, E can be found such that $x < c + d$ and $x < c' + e$. Hence, $x + d + c = d + c$, $x + c + c' = e + c'$ or $(x + d) = d$ (mod C), $(x + e) = e$ (mod C). As $\bar{C}$ is assumed to be a lattice congruence it follows that $(x + d).(x + e) = d.e$ (mod C) and $(x + d).(x + e) = x + (x + d).(x + e) = x + d.e$ (mod C). From these follow $d.e = x + d.e$ (mod C), or $d e + c'' = x + de + c''$ for some $c'' \epsilon C$, and so $x < d.e + c''$. As $d \epsilon D$, $e \epsilon E$ and $c'' \epsilon C$, $(d\,e + c'') \epsilon DE + C$ Hence, from the facts that $x < d' e + c''$, and $D.E + C$ is a μ-ideal, it follows that $x \epsilon D E + C$ also. Hence $(C+D)$ $(C+E) \subseteq C + D.E$, which, with the reverse inclusion proved before, implies $(C+D)$ $(C+E)$ $C+D E$ So the condition is necessary.

Conversely, if $C + D.E = (C+D)$ $(C+E)$ for all D, E from K_μ, the congruence modulo the μ-ideal C is a lattice congruence. We know it is an additive one always; so we should prove that $x = y$ (mod C) implies $x z = y.z$ (mod C), whatever z be from K Now $x = y$ (mod C) implies, in succession, $x + c = y + c$ for some c in C, $P_\mu(x) + P_\mu(c) = P_\mu(y) + P_\mu(c)$, $P_\mu(x) + C = P_\mu(x) + P_\mu(c) + C = P_\mu(y) + P_\mu(C) + C = P_\mu(y) + C$, $P_\mu(x.z) + C = P_\mu(x) \cdot P_\mu(z) + C = [P_\mu(x) + C] \cdot [P_\mu(z) + C] = [P_\mu(y) + C] \cdot [P_\mu(z) + C] = P_\mu(y) \cdot P_\mu(z) + C = P_\mu(y z) + C$. Now $x z \epsilon P_\mu(x z) \subseteq P_\mu(y.z) + C$ and

$y . z \epsilon P_\mu (y . z) \subset P_\mu (x . z) + C$; therefore elements c', c'' can be found in C such that $x . z < y \cdot z + c'$, $y \cdot z < x \cdot z + c''$. If $d = c' + c''$, $d \epsilon C$, and $x . z + d < y . z + c' + d = y . z + d < x . z + c'' + d = x . z + d$ or $x . z + d = y . z + d$ for a $d \epsilon C$, or $x . z \not\equiv y . z$ (mod C). Hence the condition is also sufficient.

A similar proof can be given when C is an α-ideal.

When the congruence modulo a μ-, (or α-), ideal C of K is a lattice congruence, then *the last residue-class of C[12] which is the residue-class containing 1, (0), is an α-, (a μ-), ideal D of K*; and elements of K congruent modulo D are also congruent modulo C. If the congruence modulo D is also a lattice congruence then the last residue class of D is an ideal, E, of the same sort as C, and elements of K congruent modulo E are also congruent modulo C. Hence E must be $\subset$ C In general E and C are different. If $E = C$ we call C a '*semi-simple*'[13] μ-, (or α-), ideal of K. The following remarks regarding these follow immediately from the definition of such ideals:

(4, 1) 'The congruence modulo a semi-simple ideal, as well as the one modulo its last residue-class, is a lattice congruence.

(4, 2) The last residue-class of a semi-simple ideal is also a semi-simple ideal (of the other type).

(For if $C = E$, the last residue class F of E, $= C$, is the same as D.)

We next consider the special form assumed by the results of this section when applied to special types of lattices.

5   LATTICE HOMOMORPHISMS AND CONGRUENCES AMONG MODULAR, DISTRIBUTIVE AND COMPLEMENTED LATTICES

We start with certain results regarding the nature of the lattices connected by lattice homomorphisms·

(5, 1) (a) *the lattice homomorph K' of a lattice, K, which is modular, distributive, or complemented is also a lattice of the same sort*; *and*

(b) *if there is an irreducible lattice homomorphism from a lattice K to a complemented lattice K', then the lattice K is also complemented.*

---

[12] I have considered in an earlier paper ("On the problem of the last residue-class .")· the last-residue-classes of ideals of a distributive lattice.

[13] The semi-simple ideals were first introduced and studied by R Vaidyanathaswamy in his paper "On the Lattice of open sets of a Topological Space"

For let a', b', c' be any elements of K', $0'$, $1'$ be the units of K, and let us choose any elements a, b, c from $f^{-1}(a')$, $f^{-1}(b')$, $f^{-1}(c')$; then if $a' > b'$ in K', and K is modular, $\overline{a+b} \cdot (b+c) = b + (a+b) \cdot c$. But $f(a+b) = a' + b' = a'$, so that it follows, from the above that $a' \cdot (b' + c') = b' + a' \cdot c'$; that is, K is modular. If K is distributive, $a \cdot (b+c) = a \cdot b + a \cdot c$ and so $a' \cdot (b' + c') = a' \cdot b' + a' \cdot c'$; that is, K' is also distributive. While if K is complemented, there is a complement b to any a from $f^{-1}(a')$, and from $a + b = 1$ and $a \cdot b = 0$ we deduce $a' + b' = 1'$ and $a' \cdot b' = 0'$. So b' is a complement of a'. Thus (a) is proved completely. If f is an irreducible lattice homomorphism from K to K' and if K' is complemented, then the element $a' = f(a)$, $a \in K$, has a complement $b' = f(b)$, $b \in K$; and from $a' + b' = 1'$, $a' \cdot b' = 0'$ we get $f(a+b) = f(1)$, $f(a \cdot b) = f(0)$ and so $a + b = 1$, and $a \cdot b = 0$ as f is irreducible. Hence b is a complement of a. This proves (b).

When K *is a modular lattice*, it is known that an element of K is distributed by all finite sums in K, if it is distributed by all finite products, and *vice versa*, such elements are called 'neutral elements' of K, and they form a distributive sub-lattice of K.[14] Now it can be shown, that the lattice K_μ of μ-ideals of K (and also the lattice K_α of α-ideals of K) is *modular*, if K is a modular lattice * [For if C, D, E are in K_μ and $C > D$, then $x \in C \cdot (D + E)$ implies $x \in C$, $x < d + e$ for $d \in D$, $e \in E$, and so $x < (d + e) \cdot (x + d)$. As $(x + d) > d$ and K is modular, $(x + d) \cdot (d + e) = d + (x + d) \cdot e$. Now $d \in D \subset C$, $x \in C$ imply $(x + d) \in C$, and so $d + (x + d) e \in D + C E$, which being a μ-ideal must also contain x, as $x < d + (x + d) \cdot e$. So $(C + D) \cdot (C + E) < D + C E$; but obviously, as $D \subset C$, $D + C E < (C + D) \cdot (C + E)$ So $(C + D) \cdot (C + E) = C + D \cdot E$; that is, K_μ is modular.] So, for a modular lattice, Theorem 2 gives.

> (5, 2) *the congruence modulo a μ-, (or α-), ideal of a modular lattice is a lattice-congruence if, and only if, the ideal is a* neutral *element of K_μ [of K_α]; and so [by (4, 1)] every* semi-simple *μ-, [or α-], ideal of K is a neutral element of K_μ [of K_α].*

A *distributive lattice* may be characterised as a modular lattice in which every element is neutral. And the lattices K_μ and K_α of μ- and α-ideals of a distributive lattice are known to be distributive.[15] So we have from (5, 2):

---

[14] See Ore's paper, "On the foundations of Abstract Algebra, I " (Ch II, § 3)

* This result has not been so far proved, to my knowledge

[15] For a proof see M H. Stone's paper on "Topological representations of a distributive lattice .. ."

(5, 3) *the congruence modulo any μ-, or α-, ideal of a distributive lattice is a lattice congruence; hence the lattice congruence modulo any pair of ideals (C, D) equals $\bar{C} + \check{D}$*

Note.—From the fact that $(\bar{C}, \check{D}) = \bar{C} + \check{D}$ for any pair of ideals, we can obtain now a characterisation of the canonical pair (P, Q) of ideals defining a regular lattice congruence, E, on a distributive lattice K in the form:

  ' *P contains every residue class modulo Q which intersects it and Q contains every residue class modulo P which intersects it.*'

The condition is obviously necessary, as $x \equiv y \pmod{Q}$ and $y \epsilon P$ or $y \equiv 0 \pmod{P}$ imply $x E 0$ (as $\bar{P}$, $\check{Q}$ are $\subseteq E$), while $x \equiv y \pmod{P}$, and $y \epsilon Q$ or $y \equiv 1 \pmod{Q}$ imply $x E 1$. Conversely, if the condition is assumed, and if $z \epsilon P$, then $y \equiv z \pmod{P}$ or $y \equiv z \pmod{Q}$ would imply $y \epsilon P$. Now $x E 0$ implies that every consecutive pair (x_{i-1}, x_i), $i = 1, \cdots n$, of a certain sequence $x = x_0, x_1 \ldots x_n, x_n = 0$, of elements of K, are congruent modulo P or modulo Q. As $x_n = 0 \epsilon P$, we deduce, in succession, that x_{n-1}, x_{n-2} and $x_0 = x$ are in P. So $P = e\ (0)$ and similarly $Q = e\ (1)$.

Hence given any pair of ideals (C, D) the canonical pair (P, Q) defining the regular congruence $E = \bar{C} + \check{D}$ can be obtained from (C, D) by the following transfinite construction:

  Define $C_0 = C_1$, $D_0 = D$; and for an ordinal

  $\alpha = \beta + 1$, with an immediate predecessor $\alpha - 1 = \beta$, define C_α as the union of the residue-classes modulo D_β which intersect C_β, and D_α as the union of the residue-classes modulo C_β which intersect D_β; for a limiting ordinal ω define C_ω as the union of all C_α for $\alpha < \omega$, and D_ω as the union of all D_α for $\alpha < \omega$. Then the sets C_α and D_α are μ- and α-ideals and increase with α. As K has a fixed cardinal, they cannot increase indefinitely. So there is an α, and also a least α, such that $C_{\alpha+1} = C_\alpha$ and $D_{\alpha+1} = D_\alpha$. We take $P = C_\alpha$ and $Q = D_\alpha$.

We consider next the congruence theory for *complemented modular lattices*. The existence of complements effects a considerable simplification of the theory. For we now find that:

(5, 4) *if E is any lattice congruence on a complemented modular lattice K, and $e\ (0) = C$, $e\ (1) = D$, then $E = \bar{C} = \check{D} = \bar{C} + \check{D} = (\bar{C}, \check{D})$; that is, all lattice congruences are also regular additive-, regular multiplicative- and regular lattice-congruences.*

This result can be proved by using a result due to Birkhoff,[16] that " for a lattice congruence E on K, xEy implies $x + y = x \cdot y + t$, for some t in $C = e(0)$ ". For it follows from this that xEy implies $x + y = x + (x + y)$ $= x + (x \cdot y + t) = x + t$, and $x + y = y + (x + y) = y + (x \cdot y + t) = y + t$, so that $x + t = y + t$ for a t in C, so $x \equiv y \pmod{C}$. So $E \subset \bar{C}$, while we found earlier that $\bar{C} \subset E$. So $E = \bar{C}$. By duality, $E = \check{D}$ follows. And as E is itself a lattice-congruence $E = \bar{C} = \check{D} = \bar{C} + \check{D} = (\bar{C}, \check{D})$.

This result leads to the following important consequences relating to homomorphisms between modular lattices and complemented modular lattices:

(5, 5) *A lattice homomorphism between two complemented modular lattices E on K, is always regular*

(5, 6) *A lattice homomorphism, f, from a complemented modular lattice, K, to any other lattice, K', reduces to an isomorphism if f is an irreducible additive-, an irreducible multiplicative- or an irreducible lattice-homomorphism.*

For if E is the associated lattice congruence $E(f)$ on K, the irreducibility implies either $C = P_\mu(0)$ or $D = P_\alpha(1)$ or both, and so $\bar{C} = I$, or $\check{D} = I$ or both; as $E = \bar{C} = \check{D}$, $E = I$ is true in all cases, and hence f is an isomorphism

(5, 7) *A lattice homomorphism, f, form a modular lattice, K, with units to a complemented modular lattice, K', is necessarily regular*

For if $h \cdot g$ is the resolution of f into regular and irreducible parts, $g(K) = K''$ must be a *modular* lattice as K is modular [by (5, 1), (a)], and K'' must be *complemented*, [by (5, 1), (b)], as K' is complemented and h is an irreducible lattice homomorphism from K'' to K'. So, by (5, 5), h must be regular. As it is also irreducible, it must reduce to an isomorphism; so $f = h \cdot g$, must be of the same type as g; that is, it must be regular.

(5, 8) *The semi-simple μ-, [α-], ideals of a complemented modular lattice K are the same as the neutral elements of K_μ [of K_α].*

For, we saw earlier [in (5, 2)], that any semi-simple μ-ideal of a modular lattice, K, is a neutral element of K_μ. If K is also complemented; and C is a neutral element of K_μ, by Theorem 2, $\bar{C}$ is a lattice congruence. So, by (5, 4), $\bar{C} = \check{D}$, where $D =$ the last residue-class of C Hence, it follows

---

[16] See Birkhoff's " Lattice Theory " (Theorem 4·4 in Ch IV).

that $c\widetilde{D}0$ if, and only if, $c\widetilde{C}0$ or $c\epsilon C$, that is C is the last residue-class of D. Hence C is a semi-simple μ-ideal. Dually any neutral element of K_a may be shown to be a semi-simple a-ideal.

Finally we consider congruences on a *Boolean algebra*. As a Boolean algebra is a complemented, distributive lattice and so also a complemented modular lattice, our previous results lead to the following conclusions:

    (5, 9) *For a Boolean algebra K, the lattice congruences and all three types of regular congruences coincide. The only non-regular congruences possible are additive and non-multiplicative ones or multiplicative and non-additive ones; further every μ-, [or a-], ideal of a Boolean algebra is semi-simple and a neutral element of K_μ, [of K_a].*

6. THE CLOSURE OF A DISTRIBUTIVE LATTICE FOR PRODUCT-COMPLEMENTATION

We obtain here a characterisation of those distribution lattices in which every element has a product-complement using the congruence theory

When a distributive lattice K is closed for product-complementation it is known[17] that:

    the normal elements of K, i e, elements c for which $c = c''$, form a Boolean algebra N with the same multiplication as in K; the sum $a + b$ of any two of the elements in N is equal to $(a + b)''$. And $(a \cdot b)' = (a' + b')''$, $(a + b)' = a' \cdot b'$, $0' = 1$, $1' = 0$ and $x < x''$ for all x.

So if we now define $f(x)$, for any x in K, to be equal to x'', f is a lattice homomorphism from K to N, and the subset $f^{-1}(x'')$ contains x'' as its greatest element. By result (5, 7), since the distributive lattice K is also modular, and the Boolean algebra N is also a complemented modular lattice, it follows that f should be regular. So N must be isomorphic to K/E, where $E = E(f)$ is a regular lattice congruence and so $= \widetilde{C} + \widetilde{D}$, $C = e(0)$, $D = e(1)$. Now $c\epsilon C$ or $f(c) = 0 =$ the zero of N (and of K), implies $c'' = 0$, or $c' = c''' = 0'' = 1$ or $c = c' \cdot 1 = c' \cdot c' = 0$; so $C = P_\mu(0)$. While if $d\epsilon D$, $f(d) = 1 =$ the one of N (and of K), and so $d'' = 1$ or $d' = d''' = 1' = 0$ or $d\epsilon \pi_a^{18} =$ the a-ideal of elements x of K for which

$x' = 0$. So $D = \pi_a$, and $\bar{C} + \check{D} = I + \check{D} = \check{D}$ So N is isomorphic to $K_1/E = K/\check{D}$ K_1/π_a. Thus, as N is a Boolean algebra, so is K_1/π_a. Thus we have :

(6, 1) (a) K_1/π_a *is a Boolean algebra*; *and*

(b) *each residue-class of K modulo* π_a (i e., *each* c (x) *or* f^{-1} (x″)) *contains a maximal element*,

if K is closed for product-complementation

We shall now show that the necessary conditions (a), (b) are also sufficient for K to be closed for product-complementation For assuming these, if $c \epsilon K$ and D is the element of K_1/π_a which is the Boolean-complement of $C =$ the residue-class containing c, then it is also the product-complement of C. So $C \cdot D =$ zero of $K_1/\pi_a = P_\mu$ (0), while C $E = P_\mu$ (0), for any E in K, would imply $E < D$ If now we choose d to be the maximal element of the residue-class D, then as $c \cdot d \epsilon C D$. So $c \cdot d = 0$, while $c \cdot e = 0$ would imply $C \cdot E \div P_\mu$ (0), if $e \epsilon E$. This implies $E < D$ or $E + D = D$ As $(e + d) \epsilon E + D = D$, and d is the maximal element of D, it follows that $(e + d) < d$ and so $e < d$. Hence d is the product-complement of c So " *the conditions* (a), (b) *are necessary and sufficient in order that K be closed for product-complementation* "

BIBLIOGRAPHY

Birkhoff, G   " On the structure of Abstract Algebras," *Proc Camb Phil Soc*, 1935, 31.

————   " Lattice Theory," *Am Math Soc , Collog Publ*, 25.

Dubreil, P , and M. L Dubreil Jacotin   " Theorie algebrique desr relations d'equivalence," *Jour. de Math* , 1939, 18.

Krishnan, V S   " The problem of the last-residue-class in the distributive lattice," *Proc Ind Acad Sci* , 1942, 16.

————   " On Binary relations, Congruences and Homomorphisms," *Jour. of Madras University* (Science Section), Vol XVI, No. 1 (1944).

————   " Congruences and Homomorphisms in General Algebra," to appear in the *Math Student* for March 1945.

MacNeille, H. M   " Partially ordered sets," *Trans. Am Math Soc.*, 1937, 42.

Ore, O   " On the foundations of Abstract Algebra, I," *Annals of Math* , 1935, 36.

Stone, M H.   " The theory of Representations for Boolean Algebras," *Trans Amer. Math Soc* , 1936, 40.

————   " Topological Representations of Distributive Lattices and Brouwerian Logics," *Cas. Mat. Fys.*, 1937, 67.

Tarski, A   " Calculus of Relations," *Jour Symbolic Logic*, 6, No. 3.

Vaidyanathaswamy, R   " On the lattice of open sets of a topological space," *Proc. Ind Acad Sci* , 1942, 16.

STUDIES ON THE DEPENDENCE OF OPTICAL ROTATORY POWER ON CHEMICAL CONSTITUTION

Part XXIV. The Rotatory Dispersion of Stereoisomeric 4-Chloro-o-Toluidino-, 5-Iodo-o-Toluidino- and 3-Nitro-p-Toluidino-Methylene-Camphors

By Bawa Kartar Singh and Ram Kumar Tewari

(Chemistry Department, University of Allahabad)

In the present paper the investigation of the rotatory dispersion of the condensation products of oxymethylenecamphors (d, l, dl) with 4-chloro-o-toluidine, 5-iodo-o-toluidine, and 3-nitro-p-toluidine is described.

In our previous studies[1] in this series Pasteur's Law of Molecular Dissymmetry, according to which the d- and l-forms of a substance possess identical physical properties as regards their magnitude, has been found to hold good. Our present measurements of rotatory dispersion, given in Tables II–IV, further support this generalisation: the values of optical rotatory power in different solvents of d- and l-forms of the compounds described in this paper (Tables II–IV) are identical within the limits of experimental error. In such measurements of rotatory dispersion, the maximum error allowed in the observed angle of rotation is about 0·02°. Out of 358 observations recorded in this paper in as many as 294 cases the difference between the observed and the calculated values of specific rotation corresponds to a deviation of 0·02° or less in the observed angle of rotation, and in as many as 45 cases this deviation lies between 0·02° and 0·03°. Only in 19 cases, all for Hg$_{4358}$ (Mercury violet)—a difficult line to read—this difference lies between 0·03° and 0 06°. All these are, however, of the nature of casual experimental errors.

INFLUENCE OF CHEMICAL CONSTITUTION ON THE ROTATORY DISPERSION

Rotatory dispersions may be classified as "Simple" or "Complex" according as they can, or cannot, be expressed by Drude's one-term equation, $(\alpha) = \dfrac{K}{\lambda^2 - \lambda_0^2}$. The condensation products of oxymethylene-camphors with aromatic mono-amines, described here, were found to obey the simple dispersion formula exactly. On plotting $\dfrac{1}{[\alpha]}$ against λ^2 exact

straight lines were obtained (Fig 1). This is a good proof of the rotatory dispersion being simple, but we have applied the more stringent numerical
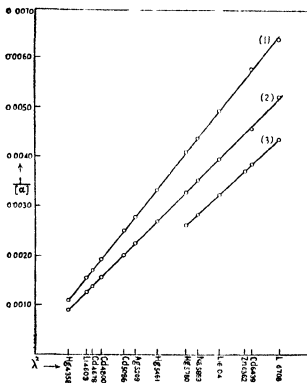
Fig. 1

(1) 5-Iodo-*o*-toluidinomethylene-*d*-camphor in benzene
(2) 4-Chloro-*o*-toluidinomethylene-*d*-camphor in ethyl alcohol
(3) 3-Nitro-*p*-toluidinomethylene-*l*-camphor in methyl alcohol

test given in Tables II–IV. The differences between the observed specific rotatory power (*o*) and that calculated (*c*) from the dispersion equations are within the experimental error allowed in such measurements as mentioned already. For the sake of economy of space these differences (*o*–*c*) are not given in these tables.

EFFECT OF THE NATURE OF THE SUBSTITUENT ON THE ROTATORY POWER

In the present investigation the effect of the NO_2 and the CH_3 groups on the rotatory power has been studied   In the following discussion the NO_2 group is regarded as positive and the CH_3 group as negative in

A2

Bawa Kartar Singh and Ram Kumar Tewari

accordance with the following polar series[a] deduced from inductive capacities·

$$\overset{-}{OH},\ Cl,\ Br,\ I,\ C_2H_5,\ \overset{-}{CH_3},\ \overset{+}{H},\ CO_2H,\ CHO,\ CO \cdot CH_3,\ CN,\ \overset{+}{NO_2}$$

TABLE I

Structural formulae	[a] 35°C Hg_{5461}					
	MeOH (31·2)†	EtOH (25·8)†	Acetone (21·5)†	Pyridine (12·4)†	Chloroform (5 2)†	Benzene (2·28)†
^{a}I C₉H₁₄ ⟨C=CH–NH–⟩Cl, CO	388 5° (63 14)	384·7° (62·47)	388 0° (63 65)	374·4° (63·70)	381·4° (61 22)	363·6° (60 73)
II C₉H₉ ⟨C=CH–NH–⟩Cl, CH₃, CO	386·0 (62 6)	378·0 (60 7)	380·0 (62 5)	390·0 (63 6)	373 0 (60 4)	361·0 (58·5)
^{b}III C₉H₁₁ ⟨C=CH–NH–⟩I, CO	338·1 (58 99)	(325·9) (54·25)	326 5 (55 22)	318·4 (54 92)	300·0 (54 46)	258 6 (47 82)
IV C₉H₁₁ ⟨C=CH–NH–⟩I, CH₃, CO	326·0 (50 8)	320 0 (49 40)	324 0 (52 30)	334·0 (53 6)	325·0 (50·5)	304·0 (48·78)
^{c}V C₉H₁₄ ⟨C=CH–NH–⟩NO₂, CO	493 1* (57 80)		468·1* (59·07)	424 8* (72·06)	484 6* (45 54)	399 2 (50 26)
VI C₉H₁₄ ⟨C=CH–NH–⟩CH₃, CO	492·0* (65·46)	459·5* (62·44)	464 1* (60·26)	416 4* (67·32)	458·5* (64·16)	390·0 (59·43)
^{d}VII C₉H₁₄ ⟨C=CH–NH–⟩CH₃, CO	165 0 (79 56)	440 8 (80 13)	425·8 (78·77)	401·6 (74·15)	401·6 (74·15)	355·4 (66·85)
^{d}VIII C₉H₁₄ ⟨C=CH–NH–⟩H, CO	480·0 (86·78)	451·3 (81 83)	448·9 (83·08)	433·2 (81·21)	424 6 (78·57)	367·1 (70 7)

a Singh and Bhaduri, *Proc Ind Acad Sci*, 1937, 6 A, 340
b Singh and Bhaduri, *ibid*, 1939, 10 A, 159
c Singh and Barat, *J Indian Chem Soc*, 1940, 17, 1
d Singh, Bhaduri and Barat, *ibid*, 1931, 8, 345
† Dielectric constant of the solvent
* Calculated value from dispersion formula

Now, since the polar effect of a substituent group is traceable in optical activity,[3] the NO₂ group being positive, should increase the rotatory power of the parent compound. This is supported by the following observations (Table I): the rotatory power of 3-nitro-p-toluidinomethylenecamphor (VI)

is higher than that of *p*-toluidinomethylenecamphor (VII) in all the solvents; the rotatory power of *o*-nitro-anilinomethylenecamphor (V) is higher than that of anilinomethylenecamphor (VIII) in all solvents except pyridine, in which the reverse obtains. On the other hand, the CH_3 group, being negative, should decrease the rotatory power of the parent compound. This is supported by the following observations (Table I): the rotatory power of 4-chloro-*o*-toluidinomethylenecamphor (II) is lower than that of *m*-chloro-anilinomethylenecamphor (I) in all the solvents except pyridine, in which it is higher; the rotatory power of 3-nitro-*p*-toluidinomethylene-camphor (VI) is lower than that of *o*-nitroanilinomethylenecamphor (V) in all the solvents; the rotatory power of 5-iodo-*o*-toluidinomethylenecamphor (IV) is lower than that of *p*-iodo-anilinomethylenecamphor (III) in three solvents but higher in pyridine, chloroform and benzene; the rotatory power of *p*-toluidinomethylenecamphor (VII) is lower than that of anilino-methylenecamphor (VIII) in all the six solvents.

It will be thus seen that, except for minor deviations above mentioned, the polar effect of a substituent group in a compound is clearly traceable in its rotatory power.

Effect of the Nature of the Solvent on the Rotatory Power

The specific rotatory power of these compounds for Hg_{5461} in six solvents is given in Table I. The sequences of decreasing rotatory power are as follows: 4-*chloro-o-toluidinomethylenecamphor* (II): pyridine > methyl alcohol > acetone > ethyl alcohol > chloroform > benzene; 5-*iodo-o-toluidinomethy-lenecamphor* (IV) pyridine > methyl alcohol > chloroform > acetone > ethyl alcohol > benzene; 3-*nitro-p-toluidinomethylenecamphor* (VI): methyl alcohol > acetone > ethyl alcohol > chloroform > pyridine > benzene In the above-mentioned three compounds the sequence of decreasing or increasing rotatory power does not run strictly parallel with that of the dielectric constants of the solvents (shown in brackets), namely, methyl alcohol (31·2) > ethyl alcohol (25 8) > acetone (21 5) > pyridine (12·4) > chloroform (5 2) > benzene (2·28) In spite of this, some parallelism can, however, be traced between the rotatory power of these compounds and the dielectric constant of the solvent in which the rotatory power is determined   the rotatory power of these compounds is lowest in benzene which has the lowest dielectric constant   Again, in methyl alcohol, which has the highest dielectric constant, the rotatory power is highest except in the case of 4-chloro-*o*-toluidinomethylenecamphor (II) and 5-iodo-*o*-toluidinomethylene-camphor (IV) (Table I)   In these cases the rotatory power is highest in pyridine which has a comparatively low value for its dielectric constant.

The above-mentioned sequences of decreasing rotatory power in different solvents are derived from the rotatory power data for Hg_{6461} (Table I). The choice of this wave-length is purely arbitrary as different sequences are obtained with other wave-lengths. For example, in the case of 3-nitro-p-toluidinomethylenecamphor (VI) the sequence for Na_{5893} is methyl alcohol > chloroform > ethyl alcohol, acetone > pyridine > benzene, whereas that for Hg_{6461} is methyl alcohol > acetone > ethyl alcohol > chloroform > pyridine > benzene. Again in the case of 5-iodo-o-toluidinomethylene-camphor (IV) the sequence for Li_{6708} is pyridine > chloroform > acetone > methyl alcohol > ethyl alcohol > benzene, whereas that for Hg_{6461} is pyridine > methyl alcohol > chloroform > acetone > ethylalcohol > benzene This shows that the sequence of the observed rotatory power in different solvents varies with the wave-length. It is, therefore, necessary for any strict comparison of rotatory power of a series of compounds that the effects of dispersion should be eliminated. This elimination is neither very easy nor very safe when the dispersion is complex; but when a linear relation is found to hold good, as in the case of compounds we have investigated extrapolation is both simple and accurate In this case when the simple dispersion formula holds good, the effects of dispersion can be eliminated completely by using the rotation-constant (K) of the one-term equation of Drude as a measure of the absolute rotatory power of the medium It refers to a wave-length λ, where $\lambda^2 - \lambda_0^2 = 1$ square micron, and is not very much greater than 10,000 Å U. The longest observed wave-length in our measurements is Li_{6708} and an extrapolation from it to about 10,000 Å U. is easily permissible in view of the linear nature of the dispersion equations obtained from these measurements We have, therefore, also given in brackets (Table I) the values of K, the rotation-constant, as a measure of the absolute rotatory power of the substances

It will be seen that the value of K (Table I) is lowest for benzene except in the case of 3-nitro-p-toluidinomethylene camphor (VI) where its value is the lowest in pyridine which has a higher dielectric constant than that of benzene. Pyridine is anomalous as in other cases it gives much higher values of K than the position of its dielectric constant in the sequence warrants it

It would, therefore, seem more rational to compare the rotatory power of a substance with the dielectric constant of its solution, and not of the solvent in which the rotatory power is determined. We have used the values of the dielectric constants of the solvents in these comparisons because we have not at our disposal the values of the dielectric constants of the solutions.

EXPERIMENTAL

Oxymethylene-*d*-camphor was prepared by the method of Bishop, Claisen and Sinclair.[4] The *l*-isomer was prepared from *l*-camphor (obtained from *l*-isoborneol) in the same way and exhibited properties similar to those of its *d*-isomeride.

General Method of Preparation.—The dextro-enantiomorphs were prepared by adding oxymethylene-*d*-camphor (1 mol proportion), dissolved in ethyl alcohol, to the solution of the free base (1 mol. proportion) in glacial acetic acid, when a precipitate separated at once or on keeping. It was then repeatedly recrystallised from ethyl alcohol.

The lævo- and racemic-isomers were prepared in the same way as the corresponding dextro-compounds and had similar crystalline form and solubility.

4-*Chloro-o-toluidinomethylene-d-camphor*, m p 121-22° C, was obtained as crystals with yellow tinge. It is very soluble in acetone, chloroform, benzene and pyridine, less so in methyl and ethyl alcohols, and insoluble in water (Found Cl, 11 50; N, 4 86 $C_{18}H_{22}ONCl$ requires Cl, 11·68; N, 4 61 per cent)

4-*Chloro-o-toluidinomethylene-l-camphor* melts at 121-22° C. (Found· Cl, 11 57. $C_{18}H_{22}ONCl$ requires Cl, 11 68 per cent.)

4-*Chloro-o-toluidinomethylene-dl-camphor* melts at 116-17° C (Found, Cl, 11 84 $C_{18}H_{22}ONCl$ requires Cl, 11·68 per cent.)

5-*Iodo-o-toluidinomethylene-d-camphor*, m p 141-42° C, was obtained as silky needles It is very soluble in acetone, chloroform, benzene and pyridine, moderately soluble in methyl and ethyl alcohols, and insoluble in water. (Found. N, 3 20, I, 32 25 $C_{18}H_{22}ONI$ requires N, 3 55, I, 32 11 per cent)

5-*Iodo-o-toluidinomethylene-l-camphor* melts at 141 42° C. (Found I, 32·02 $C_{18}H_{22}ONI$ requires I, 32 11 per cent)

5-*Iodo-o-toluidinomethylene-dl-camphor* melts at 161-62° C (Found: I, 32 23. $C_{18}H_{22}ONI$ requires I, 32 11 per cent)

3-*Nitro-p-toluidinomethylene-d-camphor*, m p 195-96° C was obtained as shining orange-red rectangular plates It is very soluble in chloroform and pyridine, less so in acetone and benzene, sparingly soluble in methyl and ethyl alcohols, and insoluble in water. (Found N, 8·70. $C_{18}H_{22}O_3N_2$ requires N, 8·92 per cent)

3-*Nitro-p-toluidinomethylene-l-camphor* melts at 195-96° C. (Found. N, 8·70 $C_{18}H_{22}O_3N_2$ requires N, 8·92 per cent.)

TABLE II

4-Chloro-o-toluidinomethylenecamphors

Solvent		Benzene	Chloroform	Ethyl alcohol	Acetone	Methyl alcohol	Pyridine
Concentration { d / l } in gm/100 cc		0·5000 / 0·5000	0·5000 / 0·5000	0·5000 / 0·5000	0·5000 / 0·5000	0·5000 / 0·5000	0·5000 / 0·5000
Calculated [α] { $\frac{k}{\lambda^2 - \lambda_0}$ }		58·5 $\lambda^2-0\cdot1358$ 0·3684	60·4 $\lambda^2-0\cdot1369$ 0·3700	60·7 $\lambda^2-0\cdot1372$ 0·3704	62·5 $\lambda^2-0\cdot1344$ 0·3666	62·6 $\lambda^2-0\cdot1355$ 0·3681	63·6 $\lambda^2-0\cdot1348$ 0·3672
Line λ		Obs. [α] d / l	Obs [α] d / l	Obs [α] d / l	Obs [α] d / l	Obs [α] d / l	Obs. [α] d / l
Hg$_{4358}$	:	+1075·0° / 1084·0°	+1141·0° / 1132·0°	+1145·0° / 1146·0°	+1121·0° / 1129·0°	+1154·0° / 1153·0°	+1158·0° / 1149·0°
Li$_{6708}$	:	772·0 / 788·0	808·0 / 804·0	812·0 / 816·0	810·0 / 806·0	823·0 / 822·0	828·0 / 822·0
C$_{6563}$	:	706·0 / 702·0	738·0 / 739·0	746·0 / 741·0	742·0 / 740·0	753·0 / 752·0	758·0 / 754·0
C$_{6438}$	:	620·0 / 618·0	648·0 / 644·0	653·0 / 649·0	653·0 / 649·0	658·0 / 658·0	657·0 / 664·0
C$_{6362}$	:	477·0 / 474·0	495·0 / 498·0	499·0 / 498·0	505·0 / 505·0	510·0 / 507·0	512·0 / 513·0
Ag$_{5461}$	:	454·0 / 430·0	451·0 / 451·0	455·0 / 454·0	435·0 / 459·0	469·0 / 483·0	466·0 / 468·0
Hg$_{4916}$	:	161·0 / 309·0	373·0 / 375·0	376·0 / 378·0	305·0 / 280·0	380·0 / 284·0	398·0 / 388·0
Hg$_{4358}$	:	294·0 / 297·0	304·0 / 308·0	310·0 / 307·0	292·0 / 311·0	314·0 / 315·0	321·0 / 321·0
N$_{4861}$	:	275·0 / 279·0	286·0 / 285·0	288·0 / 290·0	281·0 / 293·0	294·0 / 297·0	399·0 / 300·0
N$_{4658}$	:	246·0 / 249·0	258·0 / 255·0	256·0 / 259·0	235·0 / 206·0	236·0 / 286·0	366·0 / 299·0
L$_{4358}$	:	308·0 / 312·0	217·0 / 216·0	221·0 / 217·0	201·0 / 221·0	222·0 / 226·0	229·0 / 226·0
Li$_{4132}$	:	184·0 / 188·0	191·0 / 194·0	192·0 / 196·0	196·0 / 196·0	201·0 / 198·0	200·0 / 201·0
		No mutarotation	No mutarotation	No mutarotation	No mutarotation	No mutarotation	No mutarotation

TABLE III

5-Iodo-o-toluidinomethylenecamphors

Solvent	Benzene		Ethyl alcohol		Chloroform		Acetone		Methyl alcohol		Pyridine	
Concentration $\begin{cases} d \\ \lambda_0 \end{cases}$ in gm./100 c.c.	0·5000		0·5000		0·5000		0·5000		0·5000		0·5000	
	0·5000		0·5000		0·5000		0·5000		0·5000		0·5000	
Calculated $[\alpha]$ $\begin{cases} \\ \lambda_0 \end{cases}$	48·76 $\pm \overline{x^2 - 0\cdot1374}$		49·40 $\pm \overline{x^2 - 0\cdot1432}$		50·5 $\pm \overline{x^2 - 0\cdot1442}$		52·36 $\pm \overline{x^2 - 0\cdot1365}$		50·8 $\pm \overline{x^2 - 0\cdot1417}$		53·6 $\pm \overline{x^2 - 0\cdot1384}$	
	0·3707		0·3784		0·3771		0·3865		0·3764		0·3720	
Line a	Obs	$[\alpha]$	Obs	$[\alpha]$	Obs	$[\alpha]$	Obs	$[\alpha]$	Obs	$[\alpha]$	Obs	$[\alpha]$
	d		*d*		*d*		*d*		*d*		*d*	
Hg_{5456}	+932·0°	−931·0°	+722·0°	−718·0°	+1080·0°	−1051·0°	+963·0°	−894·0°	+727·0°	−723·0°	+1043·0°	−1034·0°
Li_{6708}	857·0	857·0	651·0	650·0	728·0	724·0	663·0	653·0	660·0	656·0	732·0	732·0
Cd_{6488}	900·0	596·0	568·0	565·0	661·0	660·0	638·0	634·0	572·0	571·0	668·0	664·0
Cd_{4800}	526·0	522·0	430·0	429·0	571·0	571·0	559·0	559·0	536·0	535·0	581·0	581·0
Cd_{5086}	400·0	403·0	434·0	432·0	527·0	530·0	448·0	444·0				
Ag_{5209}	366·0	363·0	387·0	387·0	393·0	393·0	387·0	390·0	391·0	393·0	403·0	405·0
Hg_{5461}	304·0	302·0	317·0	317·0	326·0	323·0	334·0	332·0	336·0	335·0	334·0	337·0
Hg_{5780}	246·0	249·0	259·0	257·0	282·0	285·0	284·0	284·0	283·0	283·0	275·0	272·0
Na_{5893}	231·0	231·0	241·0	243·0	245·0	245·0	249·0	247·0	249·0	248·0	255·0	256·0
Hg_{5770}	206·0	206·0	213·0	214·0	221·0	221·0	220·0	223·0	218·0	222·0	225·0	229·0
Cd_{6439}	176·0	175·0	180·0	178·0	187·0	187·0	190·0	184·0	187·0	184·0	196·0	198·0
Li_{6708}	156·0	154·0	162·0	163·0	166·0	166·0	166·0	169·0	164·0	166·0	174·0	171·0
	No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation	

TABLE IV

3-Nitro-p-toluidinomethylenecamphors

Solvent	Benzene		Pyridine		Ethyl alcohol		Chloroform		Acetone		Methyl alcohol	
Concentration (c / in gm l/100 c c l/	0·1000		0·1000		0·1000		0·1000		0·1000		0·1000	
	0·1000		0·1000		0·1000		0·1000		0·1000		0·1000	
Calculated $\left[\alpha\right]\left\{\frac{[\alpha]}{c_0}\right.$	$59·45$		$57·32$		$62·44$		$64·16$		$60·26$		$63·46$	
	$\pm\ \overline{\lambda^2-0·151}$		$\pm\ \overline{\lambda^2-0·1605}$		$\pm\ \overline{\lambda^2-0·1623}$		$\pm\ \overline{\lambda^2-0·1583}$		$\pm\ \overline{\lambda^2-0·1684}$		$\pm\ \overline{\lambda^2-0·1654}$	
	0·3810		0·4006		0·4029		0·3979		0·4104		0·4067	
	Obs [α]		Obs [α]		Obs [α]		Obs [α]		Obs [α]		Obs [α]	
Line	d	l	d	l	d	l	d	l	d	l	d	l
Hg6441	+300·0°	−385·0	+330·0	335·0	+390·0	−360·0	+360·0	+365·0°	+365·0°	−363·0°	385·0°	+385·0·
H64750	310·0	310·0	310·0	310·0	333·0	340·0	345·0	340·0	335·0	340·0	365·0	360·0
N6493	295·0	290·0	305·0	270·0	300·0	300·0	300·0	295·0	320·0	295·0	320·0	315·0
L4194	290·0	265·0	275·0	250·0	290·0	255·0	250·0	265·0	290·0	250·0	290·0	275·0
Zn4833	280·0	255·0	235·0	230·0	290·0	255·0	255·0	250·0	270·0	240·0	265·0	265·0
Cd4439	280·0	225·0	220·0	230·0	250·0	245·0	245·0	245·0	246·0	240·0	225·0	230·0
L6178	300·0	200·0	300·0	200·0	215·0	220·0	215·0	220·0	210·0	215·0		
	No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation	

3-*Nitro-p-toluidinomethylene*-dl-*camphor* melts at 193-94° C.   (Found: N, 8·77. $C_{18}H_{22}O_3N_2$ requires N, 8 92 per cent.)

The rotatory power determinations were carried out in a 2-dcm. jacketed tube at 35° C. The value of λ_0 calculated from the dispersion formula is given in the tables and is expressed as μ or 10^{-4} cm.

SUMMARY

(1) The rotatory dispersion of stereoisomeric 4-chloro-*o*-toluidino-, 5-iodo-*o*-toluidino-, and 3-nitro-*p*-toluidino-methylene camphors is found, in all the six solvents, to obey the Drude's one-term equation, $[\alpha] = \dfrac{K}{\lambda^2 - \lambda_0{}^2}$; it is therefore simple.

(2) Within the limits of experimental error, the *d*- and *l*-forms of these compounds possess identical rotatory power

(3) In accordance with the polar series, deduced from specific inductive capacities, the NO_2 group is considered to possess positive polarity and the CH_3 group negative polarity Subject to minor variations, the NO_2 group is found to raise, and the CH_3 group to lower the rotatory power of the parent compound.

(4) The sequence (decreasing or increasing) of rotatory power of these compounds in the different solvents does not run strictly parallel with that of the dielectric constant of the solvent in which the rotatory power is determined.

REFERENCES

1	Singh and Bhaduri	.. *J Indian Chem Soc*, 1930, **7**, 545, 771 and subsequent papers.
2	Rule	.. *J. Chem. Soc*, 1924, **125**, 1121.
3	Singh and Bhaduri	.. *Proc Ind Acad Sci*, (A) 1937, **6**, 340 ; 1939, **10**, 359
	Betti	.. *Gazz Chem Ital.*, 1923, **53**, 424
4.	Bishop, Claisen and Sinclair	*Annalen*, 1894, **281**, 331

ALGEBRA OF THE DIRAC-MATRICES

By Harish-Chandra

(J. H. Bhabha Student, Cosmic Ray Research Unit Indian Institute of Science, Bangalore)

§ 1. The Dirac matrices γ_a $(a = 1, 2, 3, 4)$ are characterised by the commutation rules

$$\gamma_a\gamma_b + \gamma_b\gamma_a = 2\,\delta_{a\,b}. \tag{1}$$

These four matrices give rise to a set of 16 quantities

$$\left.\begin{array}{l} 1 \\ \gamma_a \\ i\gamma_a\gamma_b \quad (a \neq b) \\ i\gamma_a\gamma_b\gamma_c \quad (a, b, c \text{ all different}) \\ \gamma_1\gamma_2\gamma_3\gamma_4 \end{array}\right\} \tag{2}$$

which is closed under multiplication if we regard two quantities which differ by a numerical factor -1, i or $-i$ as essentially the same. As is well known these sixteen matrices are linearly independent and apart from equivalence possess only one four-dimensional representation which is irreducible. Several important identities concerning these matrices, which are independent of any particular representation, have been established by Pauli (1936) by making use of the well-known results following from Schur's theorem. The object of the present paper is to point out that the commutation rules of the above 15 quantities' (all excluding 1) can be expressed quite elegantly by one single formula and that the above-mentioned identities can therefore be derived directly from the commutation rules. It seems that perhaps the present method is more general and powerful than that of Pauli. The identities are obtained in a form such that the five elements of any pentad (see Eddington, 1936) can be regarded as basal elements. The use of the matrix B of Pauli is avoided so that the identities (34_1) and (34_6) of his paper can now be generalised to the case $\phi^+ \neq \psi^+$, $\phi \neq \psi$. This was not possible previously. Some new tensor identities are also obtained.

Further the present method yields quite easily the matrix determinant of a quantity composed linearly from the above sixteen matrices. As is

30

well known this determinant is independent of the representation used Eddington (1936) has already calculated it by using the rather cumbersome method of employing a particular representation. As a physical application of the evaluation of this determinant we shall consider the case of a charged particle of spin $\frac{1}{2}$ having an *explicit* spin interaction with the electromagnetic field. It will be shown that apart from quantum effects and upto the first approximation the particle behaves as if it possessed a pure magnetic dipole moment, which points either along or opposite to the magnetic field in the rest system. This magnetic moment which arises from the explicit spin interaction is to be distinguished from the usual magnetic moment of the electron which is due purely to quantum effects, and which would therefore disappear if the non-commutability of the different operators were ignored.

§ 2   For the purpose of this paper it is more convenient to multiply the γ's by i and use

$$E_a = i\gamma_a \qquad (3)$$

instead of γ_a. Therefore

$$E_a E_b + E_b E_a = -2\,\delta_{ab} \qquad (4)$$

The matrices E_1, E_2, E_3, E_4 anticommute and their squares are equal to -1. Put*

$$E_0 \equiv iE_1 E_2 E_3 E_4 \qquad (5)$$

so that

$$E_0{}^2 = -1, \quad E_a E_0 = -E_0 E_a \quad (a = 1, 2, 3, 4). \qquad (6)$$

Following Eddington we define

$$
\begin{aligned}
E_{\mu\nu} &\equiv E_\mu E_\nu & (\mu,\ \nu = 1, 2, 3, 4, 5, \mu \neq \nu) \\
E_{0\nu} &\equiv E_\nu \\
E_{\nu 0} &\equiv -E_{0\nu}
\end{aligned}
\left.\vphantom{\begin{aligned}E\\E\\E\end{aligned}}\right\} \quad (\nu = 1, 2, \cdots, 5) \qquad (7)
$$

$$E_{\nu\nu} \equiv 0 \qquad (\nu = 0, 1, \cdots 5).$$

Then the following equations hold (cf Eddington *l.c*) for μ, $\nu = 0, 1, \cdots 5$

$$E_{\mu\nu} = -E_{\nu\mu} \qquad (8a)$$

$$E_{\mu\nu}{}^2 = E_{\mu\nu} E_{\mu\nu} = -1 \; (\mu \neq \nu) \qquad (8b)$$

$$E_{\mu\nu} E_{\mu\rho} = E_{\nu\rho} \; (\mu,\ \nu,\ \rho \text{ all different}) \qquad (8c)$$

$$E_{\mu\nu} E_{\sigma\rho} = E_{\sigma\rho} E_{\mu\nu} = \mp\ iE_{\lambda\tau} \; (\mu,\ \nu,\ \sigma,\ \rho,\ \lambda,\ \tau \text{ all different}) \qquad (8d)$$

---

* The present definition of E_5 differs in sign from that of Eddington. The advantage is that now

$$E_5 = iE_1 E_2 E_3 E_4 = -i\gamma_1\gamma_2\gamma_3\gamma_4 = i\gamma_5$$

corresponding to (3) γ_5 is the same as in Pauli's paper.

A3

In (8d) the positive or the negative sign is to be chosen according as $(\mu, \nu, \alpha, \rho, \lambda, \tau)$ is an odd or even permutation of (0, 1, 2, 3, 4, 5). It is easy to see that (8) is equivalent to the single equation

$$E_{\lambda\mu} E_{\nu\rho} = -\delta_{\lambda\nu} \delta_{\mu\rho} + \delta_{\mu\nu} \delta_{\lambda\rho} + E_{\lambda\nu} \delta_{\mu\rho} - E_{\mu\nu} \delta_{\lambda\rho}$$
$$- E_{\lambda\rho} \delta_{\mu\nu} + E_{\mu\rho} \delta_{\lambda\nu} \quad \frac{1}{2} \epsilon_{\lambda\mu\nu\rho\sigma\tau} E^{\sigma\tau} \qquad (9)$$

Here $\delta_{\mu\nu}$ is the usual Kronecker's symbol

$$\delta_{\mu\nu} = \begin{cases} 1 & \mu = \nu \\ 0 & \mu \neq \nu \end{cases}$$

and $\epsilon_{\lambda\mu\nu\rho\sigma\tau}$ is antisymmetric in all 6 indices and $\epsilon_{01\,2345} = 1$. It is convenient to make the convention that the same index appearing once below and once above in the same term implies a summation. Thus for example

$$E_{\rho}{}^{\nu} E_{\nu\sigma} \qquad \sum_{\nu=0}^{5} E_{\rho\nu} E_{\nu\sigma}$$

while no summation is intended in the expression

$$E_{\rho\nu} E_{\nu\sigma}$$

In fact (9) can be looked upon as a tensor equation in a six-dimensional space whose metric tensor is $\delta_{\mu\nu}$. Equation (9) is invariant to any orthogonal transformation of this six-dimensional space, if we regard $E_{\lambda\mu}$ as an antisymmetric tensor. Also if $E_{\lambda\mu}$ is any set of fifteen E-numbers[†], antisymmetric in λ, μ and satisfying the same commutation rules as (9), then it is not difficult to prove that

$$F_{\lambda\mu} = a_{\lambda}{}^{\nu} a_{\mu}{}^{\rho} E_{\nu\rho}$$

where $a_{\lambda}{}^{\nu}$ are the coefficients of an orthogonal transformation of the six-dimensional space, i.e.,

$$\sum_{\nu} a_{\lambda}{}^{\nu} a_{\mu}{}^{\nu} = \delta_{\lambda\mu}$$
$$|a_{\lambda}{}^{\nu}| = 1$$

where $|a_{\lambda}{}^{\nu}|$ denotes the six-dimensional determinant of the transformation. Thus every matrix transformation

$$F_{\lambda\mu} \quad \Lambda E_{\lambda\mu} \Lambda^{-1}$$

is equivalent to an orthogonal transformation of the six-dimensional space. The converse is also true due to the equivalence of all four-dimensional representations

---

† Any linear combination of the E' and 1 is called an E-number (cf Eddington, l.c.) Every matrix with 4 rows and 4 columns is an E-number due to the linear independence of the E's and 1.

For future use we note the following relations which follow directly from (9):—

$$E_{\lambda\mu}\,E_{\nu\rho} + E_{\lambda\nu}\,E_{\mu\rho} \cdot - -\delta_{\lambda\nu}\,\delta_{\mu\rho} - \delta_{\lambda\mu}\,\delta_{\nu\rho} + 2\,\delta_{\mu\nu}\,\delta_{\lambda\rho} + E_{\lambda\nu}\,\delta_{\mu\rho} + E_{\mu\rho}\,\delta_{\lambda\nu}$$
$$-2\,E_{\lambda\rho}\,\delta_{\mu\nu} + E_{\mu\rho}\,\delta_{\lambda\nu} + E_{\nu\rho}\,\delta_{\lambda\mu} \qquad (10a)$$

$$E_{\sigma}{}^{\nu}\,E_{\sigma\rho} \quad 5\,\delta_{\sigma\rho} - 4\,E_{\sigma\rho} \qquad (10b)$$

Also if

$$S = s + s_{\lambda\mu}\,E^{\lambda\mu}\,(s_{\lambda\mu} = - s_{\mu\lambda}) \qquad (11a)$$

$$T \cdot\!\!-\, t + t_{\lambda\mu}\,E^{\lambda\mu}\,(t_{\lambda\mu} = -\ t_{\mu\lambda}) \qquad (11b)$$

where s, $s_{\lambda\mu}$, t, $t_{\lambda\mu}$ are ordinary numbers it follows from (9) that

$$ST = st - 2\,s_{\lambda\mu}\,t^{\lambda\mu} + (st_{\lambda\mu} + ts_{\lambda\mu} - 4\,s_{\lambda\nu}\,t^{\nu}{}_{\mu} - \frac{i}{2}\,{}_{s}{}^{\alpha\beta}\,t^{\gamma\delta}\,\epsilon_{\alpha\beta\gamma\delta\lambda\mu})\,E^{\lambda\mu} \qquad (12)$$

so that

$$ST - TS = -8\,s_{\lambda\nu}\,t^{\nu}{}_{\mu}\,E^{\lambda\mu} \qquad (13a)$$

$$ST + TS = 2\,st - 4\,s_{\lambda\mu}\,t^{\lambda\mu} + 2\,(st_{\lambda\mu} + ts_{\lambda\mu} - \frac{i}{2}\,{}_{s}{}^{\alpha\beta}\,t^{\gamma\delta}\,\epsilon_{\alpha\beta\gamma\delta\lambda\mu})\,E^{\lambda\mu} \qquad (13b)$$

In particular on choosing $S = E_{\alpha\beta}$, (13) gives

$$TE_{\alpha\beta} - E_{\alpha\beta}\,T = 4\,(t_{\alpha\lambda}\,E^{\lambda}{}_{\beta} - t_{\beta\lambda}\,E^{\lambda}{}_{\alpha}) \qquad (14a)$$

$$TE_{\alpha\beta} + E_{\alpha\beta}\,T = -4\,t_{\alpha\beta} + 2\,tE_{\alpha\beta} - it\,t^{\gamma\delta}\,\epsilon_{\alpha\beta\gamma\delta\lambda\rho}\,E^{\lambda\rho} \qquad (14b)$$

On contracting with $t^{\lambda\mu}$ (10a) yields

$$TE_{\nu\rho} + t^{\lambda\mu}\,E_{\lambda\nu}\,E_{\mu\rho} = -3\,t_{\nu\rho} + 3\,t_{\nu}{}^{\lambda}\,E_{\lambda\rho} - t_{\rho}{}^{\lambda}\,E_{\lambda\nu} + T\delta_{\nu\rho}$$
$$+\,(E_{\nu\rho} - \delta_{\nu\rho})\,t \qquad (15)$$

Multiplying (14a) by $E^{\beta}{}_{\gamma}$ on the right and using (15) we obtain

$$E_{\alpha\beta}\,TE_{\beta\gamma} = T\delta_{\alpha\gamma} + 4\,(^{\circ}{}_{\alpha\gamma} - E_{\alpha\gamma})\,t + 4\,(t_{\alpha}{}^{\beta}\,E_{\beta\gamma} - t_{\gamma}{}^{\beta}\,\Gamma_{\beta\alpha}) - 8\,t_{\alpha\gamma} \qquad (16)$$

On contracting α, γ (16) gives the well-known result

$$2\,T - E^{\alpha\beta}\,TE_{\alpha\beta} = 32\,t$$

Multiplying (14a) by $E_{\alpha\beta}$ on the right we get

$$E_{\alpha\beta}\,TE_{\alpha\beta} = -T + 4\,t_{\lambda\alpha}\,E^{\lambda}{}_{\alpha} + 4\,t_{\lambda\beta}\,E^{\lambda}{}_{\beta} - 8t_{\alpha\rho}\,E_{\alpha\beta}\,(\alpha \neq \beta) \qquad (17)$$

As is well known (*cf.* Pauli, 1936) it follows from the commutation rules (9) that the spur of $E_{\lambda\mu}$ is zero. Therefore for any four-rowed representation

$$sp\,(T) = 4\,t$$

$$sp\,(E_{\lambda\mu}\,T) = -8\,t_{\lambda\mu}$$

Also since 1, $E_{\lambda\mu}$ are 16 linearly independent matrices T in (11b) can be any arbitrary matrix of 4 rows and 4 columns. Let ψ and ϕ be any two matrices with 4 rows and 1 column and ψ^{+} and ϕ^{+} with 1 row and 4

columns   Then $\phi\phi^+$, $\psi\psi^+$, $\phi_1\phi^{+_1}$ and $\psi\phi^+$ are square matrices with 4 rows and 4 columns and we can choose T equal to any of them   We notice that for $T = \phi\phi^+$

$$t = \tfrac{1}{4}\, sp\, (T) = \tfrac{1}{4}\, \phi^+\phi \tag{18a}$$

$$t_{\lambda\mu} = -\tfrac{1}{8}\, sp\, (E_{\lambda\mu}\, T) = -\tfrac{1}{8}\, \phi^+ E_{\lambda\mu}\, \phi \tag{18b}$$

Substituting these values in (11b) and (14b) and multiplying by ψ^+ on the left and ψ on the right we obtain

$$\psi^+\phi\cdot\phi^+\psi = \tfrac{1}{4}\,\psi^+\psi\,\phi^+\phi - \tfrac{1}{8}\,\psi^+ E^{\lambda\mu}\,\psi\,\phi^+ E_{\lambda\mu}\phi \tag{19}$$

$$\psi^+\phi\cdot\phi^+ E_{\alpha\beta}\psi + \psi^+ E_{\alpha\beta}\phi\cdot\phi^+\psi = \tfrac{1}{2}\,\psi^+\psi\cdot\phi^+ E_{\alpha\beta}\phi + \tfrac{1}{2}\,\psi^+ E_{\alpha\beta}\psi\cdot\phi^+\phi$$

$$+ \tfrac{i}{8}\,\phi^+ E^{\gamma\delta}\phi\,\,\psi^+ E^{\lambda\rho}\psi\,\,\epsilon_{\alpha\beta\gamma\delta\lambda\rho} \tag{20}$$

On choosing $T = \psi\phi^+$ (16) gives in the same way

$$\psi^+ E_{\alpha\beta}\psi\,\,\phi^+ E^\beta_{\ \alpha}\psi = \psi^+\psi\,\,\phi^+\phi + \psi^+\phi\,\,\phi^+\psi - \psi^+ E_{\alpha\beta}\phi\,\,\phi^+ E^\beta_{\ \alpha}\psi \tag{21}$$

$$\psi^+ E_{\alpha\beta}\psi\cdot\phi^+ E^\beta_{\ \gamma}\psi = -\,\psi^+ E_{\alpha\gamma}\phi\cdot\phi^+\psi + \psi^+\phi\,\,\phi^+ E_{\alpha\gamma}\psi$$

$$-\tfrac{1}{2}\,\psi^+ E_{\beta\gamma}\phi\,\,\phi^+ E_\alpha{}^\beta\psi + \tfrac{1}{2}\,\psi^+ E_{\beta\alpha}\phi\,\,\phi^+ E_\gamma{}^\beta\psi,\ (\alpha \neq \gamma), \tag{22}$$

Similarly on putting $T = \phi\phi^+$ (17) gives

$$\psi^+ E_{\alpha\beta}\,\phi\,\,\phi^+ E_{\alpha\beta}\,\psi = -\,\psi^+\phi\,\,\phi^+\psi - \tfrac{1}{2}\,\psi^+ E_{\lambda\alpha}\,\phi\,\,\phi^+ E^\lambda_{\ \alpha}\,\psi$$

$$-\tfrac{1}{2}\,\psi^+ E_{\lambda\beta}\phi\cdot\psi^+ E^\lambda_{\ \beta}\psi + \psi^+ E_{\alpha\beta}\psi\,\,\phi^+ E_{\alpha\beta}\phi,\ (\alpha \neq \beta). \tag{23}$$

Now let a, b, c, d be indices which run from 1 to 4 only.   Then following Pauli (1936) we put

$$\left.\begin{aligned}
\psi^+\psi &= i\Omega_0 \\
\psi^+ E_{0a}\psi &= \psi^+ E_a\psi = i\psi^+\gamma_a\psi \equiv iS_a \\
\psi^+ E_{a5}\psi &= -\,\psi^+\gamma_a\gamma_5\psi = i\psi^+\hat\gamma_a\psi \equiv i\hat S_a \\
\psi^+ E_{ab}\psi &= -\,\psi^+\gamma_a\gamma_b\psi \equiv M_{ab}\ (a \neq b) \\
M_{aa} &= 0 \\
\psi^+ E_{05}\psi &= i\psi^+\gamma_5\psi \equiv i\Omega_5 \\
\hat M_{ab} &= \tfrac{1}{2}\,\epsilon_{abcd}\,M^{cd}
\end{aligned}\right\} \tag{24}$$

Here

$$\gamma_5 = \gamma_1\gamma_2\gamma_3\gamma_4 = E_1 E_2 E_3 E_4 = -\,iE_5$$

and

$$\hat\gamma_a = i\gamma_a\gamma_5 = \tfrac{i}{3\,!}\,\epsilon_{abcd}\,\gamma^b\gamma^c\gamma^d$$

where the tensor ϵ_{abcd} is antisymmetric in all the four indices and $\epsilon_{1234} = 1$. If the corresponding quantities constructed from ϕ^+, ϕ be distinguished by

a dash, (19) can be written in the following form.

$$\psi^+ \phi \cdot \phi' \psi = - \tfrac{1}{4} \, \Omega_0 \Omega_0' + \tfrac{1}{2} \, S_a S'^a + \tfrac{1}{4} \, \hat{S}_a \hat{S}'^a - \tfrac{1}{4} \, M_{ab} M'^{ab} + \tfrac{1}{4} \, \Omega_5 \Omega_5' \quad (25)$$

Choosing $a = 0$, $\beta = 5$ in (20) we get

$$i\psi^+ \phi \cdot \phi' \gamma_5 \psi + i\psi^+ \gamma_5 \phi \cdot \phi' \psi = - \tfrac{1}{2} \, \Omega_0 \Omega_5' - \tfrac{1}{2} \, \Omega_5 \Omega_0' + \tfrac{i}{4} \, M^{ab} \hat{M}_{ab}' \quad (26)$$

Similarly putting $a = 0$ in (21) we obtain

$$S_a S'^a + \Omega_5 \Omega_5' = - \Omega_0 \Omega_0' + \psi^+ \phi \cdot \phi' \psi \cdot \phi^+ \psi \gamma_a \psi \cdot \phi^+ \gamma_a \psi \cdot \phi^+ \gamma_5 \psi \cdot \phi^+ \gamma_5 \psi \quad (27)$$

On the other hand we get on taking $a = 5$

$$\hat{S}_a \hat{S}'^a + \Omega_5 \Omega_5' = - \Omega_0 \Omega_0' + \psi^+ \phi \cdot \phi' \psi - \psi^+ \hat{\gamma}^a \psi \cdot \phi^+ \hat{\gamma}_a \psi - \psi^+ \gamma_5 \phi \cdot \phi^+ \gamma_5 \psi \quad (28)$$

On putting $a = 0$, $\gamma = 5$ in (22) gives

$$- S_a \hat{S}'^a = - i\psi^+ \gamma_5 \phi \cdot \phi^+ \psi + i\psi^+ \gamma_5 \phi \cdot \psi^+ \phi$$

$$+ \tfrac{1}{2} \, \phi^+ \gamma_a \psi \cdot \psi^+ \hat{\gamma}^a \psi + \tfrac{1}{2} \, \psi^+ \gamma_a \psi \cdot \phi^+ \hat{\gamma}^a \psi \quad (29)$$

Also if we put $a = 0$, $\beta = 5$ in (23) we get

$$- \psi^+ \gamma_5 \phi \cdot \phi' \gamma_5 \psi = - \psi^+ \psi \cdot \phi' \phi + \tfrac{1}{2} \, S_a S'^a + \tfrac{1}{2} \, \hat{S}_a \hat{S}'^a \quad (30)$$

which is the same as equation (44 P) * From (30) and (25) we get

$$- \psi^+ \gamma_5 \phi \cdot \phi' \gamma_5 \psi - \psi^+ \phi \cdot \phi^+ \psi = \tfrac{1}{2} \, \Omega_0 \Omega_0' + \tfrac{1}{4} \, M_{ab} M'^{ab} - \tfrac{1}{2} \, \Omega_5 \Omega_5' \quad (31)$$

which corresponds to equation (43 P) Equations (26), (27), (28), (29) and (31) can be written in the following form

$$\tfrac{1}{4} \, M^{ab} \hat{M}_{ab}' - \tfrac{i}{2} \, (\Omega_0 \Omega_5' + \Omega_5 \Omega_0') = (\psi^+ \phi \cdot \phi^+ \gamma_5 \psi - \phi^+ \psi \cdot \psi^+ \gamma_5 \psi)$$

$$+ (\phi^+ \psi \cdot \psi^+ \gamma_5 \phi - \psi^+ \psi \cdot \phi^+ \gamma_5 \psi) \quad (32)$$

$$2 \, S_a S'^a = - 2 \, \Omega_0 \Omega_0' - 2 \, \Omega_5 \Omega_5' - (\psi^+ \gamma_a \phi \cdot \phi^+ \gamma^a \psi - \psi^+ \gamma_a \psi \cdot \phi^+ \gamma^a \phi)$$

$$- (\psi^+ \gamma_5 \phi \cdot \phi^+ \gamma_5 \psi - \psi^+ \gamma_5 \psi \cdot \phi^+ \gamma_5 \phi) + (\psi^+ \phi \cdot \phi^+ \psi - \psi^+ \psi \phi^+ \phi) \quad (33)$$

$$2 \, \hat{S}_a \hat{S}'^a = - 2 \, \Omega_0 \Omega_0' - 2 \, \Omega_5 \Omega_5' - (\psi^+ \hat{\gamma}_a \phi \cdot \phi^+ \hat{\gamma}^a \psi - \psi^+ \hat{\gamma}_a \psi \cdot \phi^+ \hat{\gamma}^a \phi)$$

$$- (\psi^+ \gamma_5 \phi \cdot \phi^+ \gamma_5 \psi - \psi^+ \gamma_5 \psi \cdot \phi^+ \gamma_5 \phi) + (\psi^+ \phi \cdot \phi^+ \psi - \psi^+ \psi \cdot \phi^+ \phi) \quad (34)$$

$$- 2 \, S_a \hat{S}'^a = \iota \, \{\phi^+ \gamma_5 \psi \cdot \psi^+ \phi - \psi^+ \gamma_5 \phi \cdot \phi^+ \psi\}$$

$$+ \tfrac{1}{2} \, \{\phi^+ \gamma_a \psi \cdot \psi^+ \hat{\gamma}^a \phi + \phi^+ \gamma_a \psi \cdot \psi^+ \gamma^a \phi - 2 \, \phi^+ \hat{\gamma}_a \psi \cdot \psi^+ \gamma^a \psi\} \quad (35)$$

$$\tfrac{1}{2} \, M_{ab} M'^{ab} = \Omega_0 \Omega_0' - \Omega_5 \Omega_5' - 2 \, (\psi^+ \phi \cdot \phi^+ \psi - \psi^+ \psi \cdot \phi^+ \phi)$$

$$- 2 \, (\psi^+ \gamma_5 \phi \cdot \phi^+ \gamma_5 \psi - \phi^+ \gamma_5 \phi \psi^+ \gamma_5 \psi) \quad (36)$$

---

* P refers to Pauli's paper.

Equations (32) to (36) are the generalisation of equations (34$_4$ P), (34$_1$ P), (34$_3$ P), (34$_5$ P) and (34$_2$ P) respectively. Equations (32) and (36) have already been given by Pauli as equations (47 P) and (43 P) The others were not obtained by him. It is noteworthy that we have derived the identities directly without employing the matrix B of Pauli. One more interesting identity can be derived by interchanging $\phi^\dagger$ and $\psi^\dagger$ in (23) and putting $\alpha = 0$, $\beta = 5$

$$\tfrac{1}{2}\,\phi^\dagger\gamma_a\psi\cdot\psi^\dagger\gamma^a\phi + \tfrac{1}{2}\,\phi^\dagger\gamma_a\psi\cdot\psi^\dagger\hat\gamma^a\phi = -\,\Omega_a\Omega_a' - \Omega_0\Omega_0'.$$

However on putting $\phi^\dagger = \psi^\dagger$ and $\phi = \psi$ it degenerates merely into the sum of (34$_1$ P) and (34$_3$ P).

It may be mentioned here that it is possible to derive *tensor* identities in addition to the *invariant* identities given above, by choosing other suitable sets of values for a, β and γ in the equations (20) to (22). On putting $\phi = \psi$ and $\phi^\dagger = \psi^\dagger$ the following identities are obtained

$$\hat M_{ab}\hat S^b - \Omega_0 S_a = 0 \quad [a \cdot 0,\ \beta = a \text{ in (20)}] \tag{37a}$$

$$\hat M_{ab}\hat S^b + \Omega_0\hat S_a = 0 \quad [a = a,\ \beta = 5 \text{ in (20)}] \tag{37b}$$

$$M_{ab}\Omega_b + i\Omega_0\hat M_{ab} + i\,(S_a\hat S_b - S_b\hat S_a) = 0 \quad [a = a,\ \beta = b \text{ in (20)}] \tag{37c}$$

$$M_{ab}S^b + iS_b\hat S_a = 0 \quad [a = 0,\ \gamma = a \text{ in (22)}] \tag*{*(37d)}$$

$$M_{ab}\hat S^b - iS_a S_a = 0 \quad [a \quad a,\ \gamma = 5 \text{ in (22)}] \tag{37e}$$

$$S_a S_b + \hat S_a \hat S_b + M_{ac}M'_b \quad - \delta_{ab}\Omega_0^2 \quad [a = a,\ \beta = b \text{ in (21) or (22)]}] \tag{37f}$$

The generalised identities for the case $\phi \neq \psi$ and $\phi^\dagger \neq \psi^\dagger$ can be obtained by similar substitutions and they need not be given here explicitly

§ 3. Now we shall calculate the matrix determinant of T. As is well known this determinant, which we denote by det T is the same for all four-dimensional representations of $E_{\lambda\mu}$ In fact it is equal to the independent term in the characteristic equation of T. It is therefore sufficient to determine the characteristic equation For this purpose we make use of (12) and find that

$$T - t = t_{\lambda\mu}E^{\lambda\mu}$$

$$(T - t)^2 = -2\,t_{\mu\nu}t^{\mu\nu} - \frac{i}{2}\,t^{\alpha\beta}t^{\gamma\delta}\epsilon_{\alpha\beta\gamma\delta\lambda_\rho}E^{\lambda\rho}$$

$$\{(T - t)^2 + 2\,t_{\mu\nu}t^{\mu\nu}\}^2 = -\tfrac{1}{2}\,t^{\alpha\beta}t^{\gamma\delta}\epsilon_{\alpha\beta\gamma\delta\lambda_\rho}\epsilon^{\lambda\rho\alpha'\beta'\gamma'\delta'}t_{\alpha'\beta'}t_{\gamma'\delta'}$$

$$= \frac{i}{8}\,\epsilon^{\alpha\beta\mu\nu\sigma\tau}t_{\mu\nu}t_{\sigma\tau}\,e^{i\delta\mu'\nu'\sigma'\tau'}t_{\mu'\nu'}t_{\sigma'\tau'}\epsilon_{\alpha\beta\gamma\delta\lambda_\rho}E^{\lambda\rho}$$

---

* This identity was mentioned by Prof Bhabha in a lecture.

$$= \frac{i}{8} \, \epsilon^{\alpha\beta\mu\nu\sigma\tau} t_{\mu\nu} t_{\sigma\tau} \, 16 \, (t_{\alpha\beta} t_{\lambda\rho} - t_{\lambda\beta} t_{\alpha\rho} - t_{\alpha\lambda} t_{\beta\rho}) \, \mathrm{E}^{\lambda\rho}$$

$$= 2 \, i \, \epsilon^{\alpha\beta\mu\nu\sigma\tau} t_{\mu\nu} t_{\sigma\tau} \, (t_{\alpha\beta} t_{\lambda\rho} \mathrm{E}^{\lambda\rho} - 2 \, t_{\alpha\lambda} t_{\beta\rho} \mathrm{E}^{\lambda\rho})$$

$$= 2 \, i \, \epsilon^{\alpha\beta\mu\nu\sigma\tau} t_{\alpha\beta} t_{\mu\nu} t_{\sigma\tau} \, (\mathrm{T} - t) - 4 \, i \, t_{\alpha\lambda} t_{\beta\rho} \, \epsilon^{\alpha\beta\mu\nu\sigma\tau} t_{\mu\nu} t_{\sigma\tau} \mathrm{E}^{\lambda\rho} \tag{38}$$

Now

$$t_{\alpha\lambda} t_{\beta\rho} \, \epsilon^{\alpha\beta\mu\nu\sigma\tau} t_{\mu\nu} t_{\sigma\tau} = -\tfrac{1}{3} \, t_{\lambda\rho} \epsilon^{\alpha\beta\mu\nu\sigma\tau} t_{\alpha\beta} t_{\mu\nu} t_{\sigma\tau} \tag{39}$$

(39) is easily verified for a 'tensor' $t_{\mu\nu}$ whose only non-vanishing components are t_{01}, t_{23}, t_{4}. Since by a suitable orthogonal transformation every antisymmetrical tensor $t_{\mu\nu}$ can be brought into this form, it follows that the invariant equation (39) holds for every $t_{\mu\nu}$. Also

$$\epsilon_{\alpha\beta\gamma\delta\lambda\rho} \epsilon^{\lambda\rho\alpha'\beta'\gamma'\delta'} t_{\alpha'\beta'} t_{\gamma'\delta'} = 16 \, (t_{\alpha\beta} t_{\gamma\delta} - t_{\alpha\gamma} t_{\beta\delta} - t_{\alpha\delta} t_{\gamma\beta}). \tag{40}$$

Substituting (39) and (40) in (38) we get

$$\{(\mathrm{T} - t)^2 + 2 \, t_{\mu\nu} t^{\mu\nu}\}^2 - 8 \, \{(t^{\alpha\beta} t_{\alpha\beta})^2 - 2 \, t^{\alpha\beta} t_{\beta\gamma} t^{\gamma\delta} t_{\delta\alpha}\}$$
$$= \tfrac{4}{3} \, i \, t_{\alpha\beta} t_{\gamma\delta} t_{\lambda\rho} \epsilon^{\alpha\beta\delta\lambda\rho} (\mathrm{T} - t) = 0. \tag{41}$$

Equation (41) is the characteristic equation of T. Putting T $= 0$ on the left side of (41) we obtain the term independent of T so that

$$\det \mathrm{T} = (2 \, t_{\mu\nu} t^{\mu\nu} + t^2)^2 - 8 \, \{(t^{\alpha\beta} t_{\alpha\beta})^2 - 2 \, (t^{\alpha\beta} t_{\beta\gamma} t^{\gamma\delta} t_{\delta\alpha})\}$$
$$+ \tfrac{4}{3} \, i \, t_{\alpha\beta} t_{\gamma\delta} t_{\lambda\rho} \, \epsilon^{\alpha\beta\gamma\delta\lambda\rho} t \tag{42}$$

(42) agrees with the result given by Eddington* (1936) For the purpose of the following discussion it is convenient to replace T by T' where

$$\mathrm{T}' = t + \tfrac{1}{2} \, t_{\lambda\mu} \mathrm{E}^{\lambda\mu} \tag{43}$$

so that

$$\det \mathrm{T}' = (t^2 + \tfrac{1}{2} \, t_{\mu\nu} t^{\mu\nu})^2 - \tfrac{1}{2} \, \{(t^{\alpha\beta} t_{\alpha\beta})^2 - 2 \, t^{\alpha\beta} t_{\beta\gamma} t^{\gamma\delta} t_{\delta\alpha}\}$$
$$+ \frac{i}{6} \, t_{\alpha\beta} t_{\gamma\delta} t_{\lambda\rho} \, \epsilon^{\alpha\beta\gamma\delta\lambda\rho} t \tag{44}$$

Let us now revert from $\mathrm{E}^{\lambda\mu}$ to the original matrices E_a and their products. Obviously T' can be put in the form

$$\mathrm{T}' = t + t_a \mathrm{E}^a + \tfrac{1}{2} \, t_{ab} \mathrm{E}^{ab} + \frac{i}{6} \, \epsilon_{abcd} \mathrm{E}^a \mathrm{E}^b \mathrm{E}^c \mathrm{E}^d$$
$$+ \frac{1}{24} \, s \, \epsilon_{ikcd} \mathrm{E}^a \mathrm{E}^b \mathrm{E}^c \mathrm{E}^d \tag{45}$$

Here a, b, c, d run from 1 to 4 only and t_a and s_a are four-dimensional vectors while s is a scalar From (5) we have

---

* Eddington has chosen $\mathrm{E}_b = -i\mathrm{E}_1\mathrm{E}_2\mathrm{E}_3\mathrm{E}_4$ and therefore in his case the sign of i in (42) is reversed.

$$\frac{1}{24}\ \epsilon_{abcd}\mathrm{E}^a\mathrm{E}^b\mathrm{E}^c\mathrm{E}^d = -i\mathrm{E}_5 = -i\mathbf{E}_{05} \tag{46a}$$

$$\tfrac{1}{6}\ \epsilon_{abcd}\mathrm{E}^a\mathrm{E}^b\mathrm{E}^c = i\mathrm{E}_5\mathrm{E}_d = -i\mathbf{E}_{d5} \tag{46b}$$

On comparing (43) and (45) and using (46) we find

$$\left.\begin{aligned} t_{0a} &= t_a \\ t_{ab} &= s_a \\ t_{06} &= s \end{aligned}\right\} \tag{47}$$

For brevity the following notation for any vector $\mathbf{A}_a$ or a tensor $\mathbf{B}_{ab}$ is introduced

$$|\,\mathbf{A}_a\,|^2 = \mathbf{A}_a\mathbf{A}^a \tag{48a}$$

$$|\,\mathbf{B}_{ab}\,|^2 = \tfrac{1}{2}\,\mathbf{B}_{ab}\mathbf{B}^{ab} \tag{48b}$$

Then

$$\tfrac{1}{2}\,t^{\mu\nu}t_{\mu\nu} = t_{0a}t^{0a} + |\,t_{ab}\,|^2 + t_{06}t^{06} + t_{a6}t^{a6}$$
$$= |\,t_a\,|^2 + |\,t_{ab}\,|^2 + |\,s_a\,|^2 + s^2 \tag{49}$$

Also put

$$(t^2)_{\alpha\gamma} = (t^2)_{\gamma\alpha} = t_{\alpha\beta}t_{\beta\gamma} = t_\alpha{}^0t_{0\gamma} + t_\alpha{}^a t_{a\gamma} + t_\alpha{}^5 t_{b\gamma}$$

so that

$$(t^2)_{00} = -s^2 - |\,t_a\,|^2 \tag{50a}$$

$$(t^2)_{0b} = t^a t_{ab} - ss_b \tag{50b}$$

$$(t^2)_{ab} = -t_a t_b + t_a{}^c t_{cb} - s_a s_b \tag{50c}$$

$$(t^2)_{05} = -st_a + t_a{}^b s_b \tag{50d}$$

$$(t^2)_{06} = t^a s_a \tag{50e}$$

$$(t^2)_{55} = -s^2 - |\,s_a\,|^2 \tag{50f}$$

Thus we have

$$t_{\alpha\beta}t^{\beta\gamma}t_{\gamma\delta}t^{\delta\alpha} = (t^2)_{\alpha\gamma}(t^2)^{\alpha\gamma}$$
$$= (t^2)_{00}(t^2)^{00} + (t^2)_{55}(t^2)^{55} + 2\,(t^2)_{06}(t^2)^{05} + 2\,(t^2)_{0a}(t^2)^{0a}$$
$$\quad + 2\,(t^2)_{a5}(t^2)^{a5} + (t^2)_{ab}(t^2)^{ab}$$
$$= (s^2 + |\,t_a\,|^2)^2 + (s^2 + |\,s_a\,|^2)^2 + 2\,(t^a s_a)^2 + 2\,|\,t^a t_{ab} - ss_b\,|^2$$
$$\quad + 2\,|\,t_a{}^b s_b - st_a\,|^2 + 2\,|\,t_a t_b + s_a s_b - t_a{}^c t_{cb}\,|^2 \tag{51}$$

From (44), (47), (49) and (51) we have

$$\det \mathrm{T}' = (t^2 + |\,t_a\,|^2 + |\,t_{ab}\,|^2 + |\,s_a\,|^2 + s^2)^2 - 2\,|\,t_a\,|^2 + |\,t_{ab}\,|^2 + |\,s_a\,|^2 + s^2)^2$$
$$+ (s^2 + |\,t_a\,|^2)^2 + (s^2 + |\,s_a\,|^2)^2 + 2\,(t^a s_a)^2 + 2\,|\,t^a t_{ab} - ss_b\,|^2$$
$$+ 2\,|\,t_a{}^b s_b - st_a\,|^2 + 2\,|\,t_a t_b + s_a s_b - t_a{}^c t_{cb}\,|^2$$
$$+ i\,s\,t_{ab}t_{cd}\,\epsilon^{abcd}t + 4\,i\,t_a t_b{}^c t_d\,\epsilon^{abcd}t \tag{52}$$

since

$$t_{\alpha\beta}t_{\gamma\delta}t_{\lambda\rho}\,\epsilon^{\alpha\beta\gamma\delta\lambda\rho} = 6\,t_{06}t_{ab}t_{cd}\,\epsilon^{05abcd} + 24\,t_{0a}t_{bc}t_{d6}\,\epsilon^{0abcd5}$$

Instead of E_a or γ_a which satisfy (4) or (1) respectively it is convenient to introduce the matrices a_μ ($\mu = 0, 1, 2, 3$) whose commutation rules are

$$a_\mu a_\nu + a_\nu a_\mu = 2 g_{\mu\nu}$$ (53)

where $g_{\mu\nu}$ is the usual metric tensor of flat space-time ($g_{\mu\nu} = 0$, $\mu \neq \nu$, $g_{00} = -g_{11} = -g_{22} = -g_{33} = 1$) For this purpose it is sufficient to choose $(a_1, a_2, a_3) = (E_1, E_2, E_3)$ and $a_0 = -iE_4 = \gamma_4$ From now onwards the greek indices run from 0 to 3.   We make the convention that for any tensor $A_{ab}\cdots$

$$i^n A_{(0)n} = A_{(4)n}$$ (54)

where $A_{(4)n}$ denotes that among $a, b, \cdots$ there are n indices equal to 4.   The new quantity $A_{(0)n}$ defined by (54) is obtained by replacing each index 4 by 0. Since for raising the greek indices we use the tensor $g^{\mu\nu}$ the following relation holds

$$A_{\mu\nu}\cdots \quad B^{\mu\nu}\cdots = (-1)^m A_{ab}\cdots B^{ab}\cdots$$

where m is the total number of indices $a, b, \cdots$ in each of the tensors $A_{ab}\cdots$ and $B^{ab}\cdots$ which are contracted together Also from (54)

$$\epsilon_{0123}\cdots = -\epsilon_{12'0}\cdots = i\epsilon_{1234} \cdot 1$$

Therefore we put

$$\epsilon_{\mu\nu\sigma\tau} = i\,\eta_{\mu\nu\sigma\tau}$$

where $\eta_{0123} = 1$. Thus (45) and (52) can be written as

$$T' = t - t_\mu a^\mu + \tfrac{1}{2} t_{\mu\nu} a^\mu a^\nu - \tfrac{1}{6}\,\eta_{\mu\nu\sigma\tau}\, a^\mu a^\nu a^\sigma s\tau$$
$$- \frac{1}{24}\, s\, \eta_{\mu\nu\sigma\tau}\, a^\mu a^\nu a^\sigma a^\tau t$$ (55)

$$\det T' = (t^2 - |t_\mu|^2 + |t_{\mu\nu}|^2 - |s_\mu|^2 + s^2)^2 - 2\,(-|t_\mu|^2 + |t_{\mu\nu}|^2 - |s_\mu|^2 + s^2)^2$$
$$+ (s^2 - |t_\mu|^2)^2 + (s^2 - |s_\mu|^2)^2 + 2\,(t^\mu s_\mu)^2 - 2\,|ss_\mu|^2 + i^\sigma t_{\mu\mu}|^2$$
$$- 2\,|st_\mu + t_\mu{}^\sigma s_\nu|^2 + 2\,|t_\mu t_\nu + s_\mu s_\nu + t_\mu{}^\sigma t_{\sigma\nu}|^2$$
$$- s\, t_{\mu\nu} t_{\sigma\tau}\, \eta^{\mu\nu\sigma\tau} t - 4\, t_{\mu\nu} t_{\sigma\tau}\, \eta^{\mu\nu\sigma\tau} t$$ (56)

A notation similar to (48) has been employed in (56) for greek indices also.

The above result can immediately be applied to discuss the case of a particle of spin $\tfrac{1}{2}$ having a charge- and dipole-interaction with an electro-magnetic (or meson) field. If p_μ be the energy-momentum vector of the particle, ϕ_μ the electromagnetic potentials and $F_{\mu\nu}$ the field-strengths the wave equation for the particle can be written as

$$\left\{a^\mu\,(p_\mu - g_1\phi_\mu) + \frac{i}{2}\, g_2 a^\mu a^\nu F_{\mu\nu} + m\right\}\psi = 0.$$ (57)

Here g_1 is the charge and g_2 the dipole-strength and m the mass of the particle. Our object is to determine the classical analogue of this particle. Hence we treat p_μ, ϕ_μ, $F_{\mu\nu}$ as numerical quantities commuting with each other. This corresponds to the neglect of quantum effects. As is well known the condition for the existence of a solution of (57) is that

$$\det \{\alpha^\mu \pi_\mu + \frac{i}{2} g \alpha^\mu \alpha^\nu F_{\mu\nu} + m\} = 0. \tag{58}$$

Here $\pi_\mu = p_\mu - g_1 \phi_\mu$ and we have written g instead of g_2 for simplicity (58) corresponds to the classical equation of motion of the particle. Comparing (58) and (55) we find

$$t = m$$
$$t_\mu = -\pi_\mu$$
$$t_{\mu\nu} = ig F_{\mu\nu}$$
$$s_\mu = 0, \quad s = 0$$

so that on account of (56), (58) reduces to

$$(\pi_\mu \pi^\mu - m^2 + \frac{1}{2} g^2 F_{\mu\nu} F^{\mu\nu})^2 - 4 \pi_\mu \pi^\mu (\frac{1}{2} g^2 F_{\nu\sigma} F^{\nu\sigma}) - 2 (\frac{1}{2} g^2 F_{\mu\nu} F^{\mu\nu})^2$$
$$- 4 g^2 \pi_\mu \pi^\mu F^{\mu\nu} F_{\nu\sigma} \pi^\sigma + g^4 F_\mu{}^\nu F_{\nu\sigma} F^{\sigma\tau} F_\tau{}^\mu = 0. \tag{59}$$

Now

$$F_{\mu\nu} F^{\sigma\tau} F_{\sigma\tau} \pi^\mu = 2 (\frac{1}{2} F_{\mu\nu} F^{\mu\nu})^2 + (\frac{1}{2} F_{\mu\nu} F^{*\mu\nu})^2 \tag{60}$$

where $F^{*\mu\nu}$ is the tensor dual to $F^{\mu\nu}$ and is defined by

$$F^{*\mu\nu} = \frac{1}{2} \eta^{\mu\nu\sigma\tau} F_{\sigma\tau} \tag{61}$$

Equation (60) is easily verified for the particular Lorentz-frame in which only F_{01} and F_{23} are different from zero. Since it is a tensor equation it must hold for every other frame also. Thus we obtain from (59) and (60)

$$[\pi_\mu \pi^\mu - m^2 + \frac{1}{2} g^2 F_{\mu\nu} F^{\mu\nu}]^2 + 4 \{(\frac{1}{2} g^2 F_{\mu\nu} F^{*\mu\nu})^2 - \pi_\mu \pi^\mu (\frac{1}{2} g^2 F_{\nu\sigma} F^{\nu\sigma})$$
$$- g^2 \pi_\mu \pi^\mu F^{\mu\nu} F_{\nu\sigma} \pi^\sigma = 0 \tag{62}$$

When the explicit spin interaction is absent $g = 0$ and (62) reduces to the usual classical equations of a point-charge

$$\pi_\mu \pi^\mu - m^2 = 0. \tag{63}$$

In this case

$$\pi_\mu = m \, v_\mu \tag{64}$$

where v_μ is the classical four-velocity of the particle. Since we wish to retain only terms of the lowest order in g in (62) we can substitute (64) in the terms of (62) containing g, so that on ignoring terms of the order g^2, (62) becomes

$$(\pi_\mu \pi^\mu - m^2 + \frac{1}{2} g^2 F_{\mu\nu} F^{\mu\nu})^2 = 4 m^2 g^2 (\frac{1}{2} F_{\mu\nu} F^{\mu\nu} - F_\mu F^\mu) \tag{65}$$

where $F_\mu = F_{\mu\nu} v^\nu$. Therefore

$$\pi_\mu \pi^\mu - m^2 = \pm \, 2\, mg \, \sqrt{\tfrac{1}{2} \, F_{\mu\nu} F^{\mu\nu} - F_\mu F^\mu} \qquad (66)$$

if the second and higher powers of g are neglected   Now

$$\tfrac{1}{2} F_{\mu\nu} F^{\mu\nu} - F_\mu F^\mu = \mathbf{H}^2$$

where $\mathbf{H}$ is the magnetic field in the rest system of the particle   Therefore

$$\pi_\mu \pi^\mu - m^2 = \pm \, 2\, mg \mid \mathbf{H} \mid \qquad (67)$$

For the non-relativistic case we find on putting $\pi_0 = m + \mathrm{W}$ that

$$\mathrm{W} = \frac{\pi^2}{2\, m} \pm g \mid \mathbf{H} \mid \qquad (68)$$

where $\pi = (\pi_1, \pi_2, \pi_3)$. (68) shows that in the rest system and in a weak electromagnetic field the particle manifests only a *magnetic moment* g such that the direction of the moment is either along or opposite to the magnetic component of the field.   This is precisely what is to be expected of a particle of spin $\tfrac{1}{2}$

I am thankful to Prof. H J Bhabha for helpful comments and advice.

SUMMARY

The Dirac-matrices generate an algebra consisting of sixteen linearly independent elements   A formula is given for expressing the product of any two elements as a linear combination of these sixteen   This determines the structure of the algebra completely.   It is shown that certain known identities concerning these matrices can be obtained comparatively easily by the present method.   Some new identities are also deduced.

The characteristic equation of a general element of the algebra is derived and from it an expression is obtained for the determinant of any four-dimensional matrix representing the element.   This expression is used to discuss the case of a particle of spin $\tfrac{1}{2}$ having an explicit spin interaction with the electromagnetic field   It is shown that in the classical limit $\hbar \to o$ and upto the first approximation in the interaction constant g the particle manifests only a *magnetic-moment* g in the rest system, the direction of the moment being either along or opposite to the magnetic field in the same system

REFERENCES

1   Eddington   *Relativity theory of electrons and protons*, Cambridge University Press, 1936.

2   Pauli   ,   *Ann. Inst. Poincaré*, 1936, 6 109–36.

CHARACTERS OF THE CLASSES OF THE FORM
(n_1, n_2, n_3) IN SYMMETRIC GROUPS

By T. Venkatarayudu, M.A., Ph.D., F.A.Sc.

(Department of Physics, Andhra University, Guntur)

1. Introduction

In a previous paper* the author proved that the characters of the classes (n) and (n_1, n_2) are zero except in the following cases:—

$$(1\cdot1) \qquad \chi_{(n)}^{[x, \, 1^a]} \qquad = (-1)^a \qquad\qquad x \geqslant 1$$

$$(2\cdot1) \qquad \chi_{(n_1, \, n_2)}^{[x, \, 1^a]} \qquad = (-1)^a \quad \text{when } 0 \leqslant a < n_2$$
$$= (-1)^{a-1} \text{ when } a \geqslant n_1$$
$$= (-1)^{a-1} \text{ when } a = n_2 \text{ or } n_2 - 1 \text{ only if } n_1 = n_2$$

$$(2\cdot2) \qquad \chi_{(n_1, \, n_2)}^{[x, \, y, \, 2^b, \, 1^a]} \qquad \begin{aligned} &= (-1)^{a+1} \text{ if } n_1 \neq n_2 \\ &= 2(-1)^{a+1} \text{ if } n_1 = n_2 \end{aligned} \Bigg\} \begin{aligned} &\text{when } x = n_1 - a - b - 1 \\ &\text{and } \quad y = n_2 - b + 1 \end{aligned}$$

$$(2\cdot3) \qquad \chi_{(n_1, \, n_2)}^{[x, \, y, \, 2^b, \, 1^a]} \qquad \begin{aligned} &= (-1)^a \quad \text{if } n_1 \neq n_2 \\ &= 2(-1)^a \quad \text{if } n_1 = n_2 \end{aligned} \Bigg\} \begin{aligned} &\text{when } x = n_1 - b \\ &\text{and } \quad y = n_2 - a - b \end{aligned}$$

$$(2\cdot4) \qquad \chi_{(n_1, \, n_2)}^{[x, \, y, \, 2^b, \, 1^a]} \qquad \begin{aligned} &= (-1)^a \quad \text{if } n_1 \neq n_2 \\ &= 2(-1)^a \quad \text{if } n_1 = n_2 \end{aligned} \Bigg\} \begin{aligned} &\text{when } x = n_2 - b \\ &\text{and } \quad y = n_1 - a - b. \end{aligned}$$

For $n_1 = n_2$ results $(2\cdot3)$ and $(2\cdot4)$ are identical. In quoting the above results the notation is slightly altered for the sake of uniformity. In the present paper we obtain the characters of the classes of elements containing three cycles.

2 Characters of the Classes of the Form (n_1, n_2, n_3)

If P_1, P_2, P_3 stand respectively for the totality of the partitions

(1) $[x, \, 1^a]$ $\qquad\qquad x \geqslant 1; \; a \geqslant 0$

(2) $[x, \, y, \, 2^b, \, 1^a]$ $\qquad x \geqslant y \geqslant 2; \; a \geqslant 0, b \geqslant 0$

(3) $[x, \, y, \, z, \, 3^c, \, 2^b, \, 1^a]$ $\qquad x \geqslant y \geqslant z \geqslant 3, \; a \geqslant 0, b \geqslant 0, c \geqslant 0$

we have the following

Theorem 1.—

$$\chi^{[\lambda]}_{(n_1, n_2, \cdots n_k)} = 0$$

for all partitions $[\lambda]$ not belonging to $P_1, P_2, \ldots P_k$.

The proof of the theorem follows immediately if we note that it is impossible to build regular graphs of the partitions not belonging to P_1 $P_2, \ldots P_k$ by consecutive regular applications of n_1, n_2 n_k nodes.

From the above theorem it follows that the non-zero characters of the classes (n_1, n_2, n_3) come only from partitions belonging to P_1, P_2, P_3. But this does not mean that the characters are different from zero in all the partitions of P_1, P_2 and P_3. Using the recurrence relations between S-functions† we now obtain the characters of the classes (n_1, n_2, n_3) in terms of the characters of the classes (n_1, n_2)

Theorem 2.—

$$\chi^{[\nu, 1^a]}_{(n_1, n_2, n_3)} = \alpha_1 + \beta_1$$

where

$$\alpha_1 = (-1)^{n_3 - 1} \chi^{[\nu, 1^{a-n_3}]}_{(n_1, n_2)} \text{ if } a \geqslant n_3$$

and

$$\beta_1 = \chi^{[\nu - n_3, 1^a]}_{(n_1, n_2)} \text{ if } \lambda > n_3$$

α_1 and β_1 are zero in all other cases

Using (2·1) we obtain $\chi^{[\nu, 1^a]}_{(n_1, n_2, n_3)}$

Theorem 3.—

$$\chi^{[\nu, \nu \, 2^b, 1^a]}_{(n_1, n_2, n_3)} = \alpha_2 + \beta_2 + \beta'_2 + \gamma_2 + \delta_2$$

where

$$\alpha_2 = (-1)^{n_3 - 1} \chi^{[\nu, \nu, 2^b, 1^{a-n_3}]}_{(n_1, n_2)} \text{ if } a \geqslant n_3$$

$$\beta_2 = (-1)^{n_3 - 1} \chi^{[\nu, \nu, 2^{b-n_3}, 1^{a+n_3}]}_{(n_1, n_2)} \text{ if } b \geqslant n_3$$

$$\beta'_2 = (-1)^{a+b-t-1} \chi^{[\nu, \nu, 2^t, 1^{b-t-1}]}_{(n_1, n_2)} \text{ for } t < b \text{ and}$$

$$n_3 + t = a + b + 1$$

---

† See D E Littlewood, *The Theory of Group Characters and Matrix Representations of Groups*, 1940, p 98

A3 b

$$\gamma_2 = \chi_{(n_1,\,n_2)}^{[x,\,y-n_3,\,2^b,\,1^a]} \text{ if } y \geqslant n_3 + 2$$

$$= (-1)^b \chi_{(n_1,\,n_2)}^{[x,\,1^{y-n_3+a}]} \text{ if } 0 \leqslant y - n_3 = 1 - b$$

$$= (-1)^{a+b} \chi_{(n_1,\,n_2)}^{[x,\,1^{y-n_3+b+a}]} \text{ if } y - n_3 = -(a+b)$$

$$\delta_2 = \chi_{(n_1,\,n_2)}^{[x-n_3,\,y,\,2^b,\,1^a]} \text{ if } x - n_3 \geqslant y$$

$$= (-1) \chi_{(n_1,\,n_2)}^{[y-1,\,x-n_3+1,\,2^b,\,1^a]} \text{ if } y - 1 > x - n_3 \geqslant 1$$

$$= (-1)^{b+1} \chi_{(n_1,\,n_2)}^{[y-1,\,1^{a+2b+a-n_3}]} \text{ if } y - 1 > x - n_3 = -b.$$

α_2, β_2, β_2', γ_2, δ_2 are zero in all other cases.

Using (2 1) to (2 4) $\chi_{(n_1,\,n_2,\,n_3)}^{[x,\,y,\,2^b,\,1^a]}$ is obtained

Theorem 4.—

$$\chi_{(n_1,\,n_2,\,n_3)}^{[x,\,y,\,z,\,3^a,\,2^b,\,1^a]} = \alpha_3 + \beta_3 + \gamma_3$$

where

$$\alpha_3 = (-1)^c \chi_{(n_1,\,n_2)}^{[x,\,y,\,2^{b+c+1},\,1^a]} \text{ if } z - n_3 = 2 - c$$

$$= (-1)^{b+c} \chi_{(n_1,\,n_2)}^{[x,\,y,\,2^c,\,1^{a+b+1}]} \text{ if } z - n_3 = 1 - b - c$$

$$= (-1)^{a+b+c} \chi_{(n_1,\,n_2)}^{[x,\,y,\,2^c,\,1^{a+b}]} \text{ if } z - n_3 = -(a+b+c)$$

$$\beta_3 = (-1)^{c+1} \chi_{(n_1,\,n_2)}^{[x,\,z-1,\,2^{b+c+1},\,1^a]} \text{ if } z - 1 > y - n_3 = 1 - c$$

$$= (-1)^{b+c+1} \chi_{(n_1,\,n_2)}^{[x,\,z-1,\,2^c,\,1^{a+b}]} \text{ if } z - 1 > y - n_3$$
$$= -(b+c)$$

$$= (-1)^{a+b+c+1} \chi_{(n_1,\,n_2)}^{[x,\,z-1,\,2^c,\,1^{a+b}]} \text{ if } z - 1 > y - n_3$$
$$= -(1+a+b+c)$$

$$\gamma_3 = (-1)^c \chi_{(n_1,\,n_2)}^{[y-1,\,z-1,\,2^{b+c+1},\,1^a]} \text{ if } z - 2 > x - n_3 = -c$$

$$= (-1)^{b+c} \chi_{(n_1,\,n_2)}^{[y-1,\,z-1,\,2^c,\,1^{a+b+1}]} \text{ if } z - 2 > x - n_3$$
$$= -(1+b+c)$$

α_3, β_3, γ_3 are zero in all other cases,

Using relations (2·2) to (2·4) $\chi^{[x,y,z,3^a,2^b,1^a]}_{(n_1,\,n_2,\,n_k)}$ is evaluated.

The author's thanks are due to Prof. S Bhagavantam, (Hon) D sc., for his kind help and encouragement

Summary

It is shown in this paper that the non-zero characters of the classes of the form $(n_1,\;n_2,\;\ldots\;n_k)$ come only from partitions belonging to $P_1,\;P_2,\;\ldots\;P_4$. Using the recurrence relations between S-functions the characters of the classes $(n_1,\;n_2,\;n_3)$ are expressed in terms of the known characters of the classes $(n_1,\;n_2)$

STUDIES ON THE NATURE OF THE RACEMIC MODIFICATIONS OF OPTICALLY ACTIVE COMPOUNDS

Part III. Roozeboom Solubility-Composition Isotherm for Mixtures of Active and Inactive Camphoric Acids at 35° C.

By Bawa Kartar Singh and Bal Kishore K. Nayar

(Department of Chemistry, University of Allahabad)

THE existence of racemic compounds in the solid state has long been recognized mainly as the result of investigations on their crystal structure[1] and of the freezing point curves of mixtures of the active and inactive forms.[2] But the evidence for their existence in solution or in the fused state has not been equally unequivocal. Ordinary cryoscopic methods give molecular weights identical with those of the active forms,[3] but Bruni found that the molecular weight increased on the addition of one of the active forms. Investigations on electrolytic conductivity,[5] molecular volume[6] and surface tension[7] of the racemic forms and of their optically active isomers did not yield any positive evidence for the existence of racemic compounds in solution. On the other hand Stewart[8] found that the absorption spectra of the racemic and optically active forms of tartaric acid gave indication of the existence of the racemic compound at concentrations above 14 per cent. At lower concentrations the absorption spectra of the three forms were identical. Evidence as to the existence of the racemic compound in solution has been furnished by one of us[9] from viscosity measurements of d-, l-, and dl-forms of camphor, isonitrosocamphor, camphorquinone, camphoric acid and sodium camphorate at different concentrations. A comparison of the viscosity values of the three forms at corresponding concentrations showed that the values for all the three were identical up to a certain concentration, but above this concentration, though the values for the d- and l-forms agreed as was to be expected, that for the dl-form was appreciably higher indicating the existence of racemates.

A racemic modification may exist in one of three forms in the solid state:—(i) a mechanical mixture of the d- and l-forms (conglomerate); (ii) a solid solution (mixed crystal) of the d- and l-forms; or (iii) a racemic compound of the optically active and opposite forms. Roozeboom[10] devised two methods for distinguishing between the three types.

Freezing-point Method.—A freezing point-composition diagram for mixtures of the racemic modification and the corresponding optically active forms is prepared.   A simple mixture of *d*- and *l*-isomerides would give a curve consisting of two parts with a minimum of temperature at the point of intersection (eutectic point).   The mixed-crystal type will give a continuous single curve joining the melting points of the two isomerides.   The racemic compound will give a curve consisting of 3 parts with two minima (eutectic points) and a maximum point.   Several cases illustrating this method have already been reported in Parts I and II of this series.[2(d)]

Solubility Method.—Roozeboom[10] and also Bruni[11] have theoretically discussed, from the phase rule standpoint, the solubility relationships existing between optical isomerides and their racemic mixtures, compounds or solid solutions.   The solubility-composition isotherms which they have derived theoretically had not hitherto been experimentally established nor is there any experimental data which definitely correlates the melting point curves abovementioned with the solubility curves.   In a previous communication by one of us,[2(d)] it was proposed to undertake this experimental study.   The present paper deals with the solubility measurements on camphoric acids* at 35° C.

Biochemical Method.—A third method has been developed by one of us,[12] which depends on the different actions of the optically active and opposite forms on micro- and higher organisms.   Although there is absolute identity of the enantiomorphic forms in their chemical and physical properties, their biological reactions towards living matter may be very different as has been found by Pasteur, Piutty, Cushny, Singh[13] and others.   The action of the racemic form will be generally different from those of the optically active forms; if it is a mixture the properties of the racemic form will be the mean of those of the active forms ($d > dl > l$ or *vice versa*), whereas if it is a compound its properties may be altogether different from those of the enantiomorphic modifications.   In this case, if the biological effect of the racemic form is the highest or the lowest of the three forms, then it is a compound.   It was thus possible to establish that the *dl*-modification of camphor-β-sulphonic acids and some of its salts with organic bases were true *dl*-compounds, a result which is in agreement with the deductions made from freezing-point method above mentioned.[2(d)]

EXPERIMENTAL

The *d*-, *l*- and *dl*-camphoric acids were prepared and purified by the methods described by Singh and Mahanti.[14]   The camphoric acids were

---

* A parallel investigation on camphor-β-sulphonic acids with Mr O N Perti is in progress (B.K.S.).

repeatedly crystallised from hot water till the following constants were obtained d- and l- camphoric acids M. P. 188-89° C.; $[\alpha]_{5461}^{20} = \pm 55 \cdot 8$ (0·8 per cent. aqueous solution); dl- acid M P. 202-03° C.

The measurements of solubility were made in an apparatus prepared according to the description of Campbell [15] The direction of rotation of the thermostat stirrer was frequently reversed to ensure proper agitation of the solution. The solution was made by dissolving the substances at 50–60° and then placing it in the thermostat which was maintained at 35 ±·05° C. The solution was kept stirred for about 16 hours when complete equilibrium was attained, stirring for longer periods did not produce any further change.

Seventy grams of conductivity water was taken in every case and the total amount of acid determined by titration with sodium hydroxide using phenolphthalein as indicator The solubility eutectic (isothermal invariant) point was determined by estimating the amount of the active form polarimetrically and the total acid by titration The intermediate values were determined by adding a known amount of one of the forms to a saturated solution of the other, the amount of the active form in the saturated solution being confirmed in every case by measuring the optical rotation. The results agree within experimental error, showing that the rotations are not measurably changed by the presence of the inactive form and hence the position of the invariant point is not in error. The solid in equilibrium with the solution, in the region in between the two invariant points, was examined polarimetrically after drying thoroughly in several cases. There was no measurable rotation showing the phase to be the dl-form.

DISCUSSION

The experimental results given in Tables I and II are reproduced in Figs. 1 and 2. Fig. 1 is plotted with the total solubility (grams per 100 grams of solvent) as ordinate and the percentage composition as abscissa. Fig. 2 is after Roozeboom's method of plotting three-component systems, the amount of solute being expressed in grams per 100 grams of solution. The amounts of the active form taken in plotting the graphs is that determined polarimetrically, as the composition of the invariant point was also determined in this way. In each case three curves have been obtained, indicating that the racemic form of camphoric acid is a true dl-compound.

As far as we are aware this is the first phase rule study in which Roozeboom solubility-composition isotherm giving the solubility relationship which exists between the optical enantiomorphs and their racemic form has been investigated, and the exact shape and slope of the curves determined. In the previous investigations, given in Parts I and II of this series, the melting

TABLE I

Solubility of mixtures of d- and dl-camphoric acids in grams per 100 grams of water at 35° C.

Total acids by titration	d-acid (taken)	d-acid (from opt rotation)	dl-acid (by difference)	dl-acid (taken)	Percentage composition	
					dl-acid	d-acid
0·272	0·000	0·000	0·272	Excess	100·0	0·0
0·276	0·067	0·064	0·212	,,	76·8	23·2
0·280	0·114	0·107	0·173	,,	59·5	40·5
0·290	0·171	0·165	0·125	,,	41·0	59·0
0·328	0·228	0·220	0·108	,,	30·5	69·5
0·415	0·342	0·340	0·075	,,	18·1	81·9
0·504	0·456	0·447	0·067	,,	11·5	88·5
0·649	0·598	0·594	0·055	,,	8·7	91·3
0·800	0·748	0·745	0·055	,,	6·8	93·2
0·940	Excess	0·885	0·055	,,	5·9	94·1
0·935	,,	0·885	0·050	0·051	5·4	94·6
0·920	,,	0·894	0·026	0·030	2·8	97·2
0·920	,,	0·913	0·007	0·010	1·0	99·0
0·915	,,	0·918	0·000	0·000	0·0	100·0

TABLE II

Solubility of mixtures of l- and dl-camphoric acids in grams per 100 grams of water at 35° C.

Total acid by titration	l-acid (taken)	l-acid (from opt rotation)	dl-acid (by difference)	dl-acid (taken)	Percentage composition	
					dl-acid	l-acid
0·272	0·000	0·000	0·272	Excess	100·0	0·0
0·276	0·067	0·055	0·213	,,	76·0	23·4
0·282	0·115	0·107	0·175	,,	62·0	38·0
0·313	0·200	0·193	0·120	,,	38·3	61·7
0·408	0·330	0·331	0·077	,,	18·9	81·1
0·500	0·443	0·436	0·064	,,	12·8	87·2
0·558	0·599	0·598	0·060	,,	9·1	90·9
0·696	0·646	0·640	0·056	,,	7·5	92·5
0·842	0·784	0·782	0·060	,,	7·1	92·9
0·945	Excess	0·890	0·055	,,	6·0	94·0
0·931	,,	0·899	0·032	0·041	3·4	96·6
0·918	,,	0·918	0·000	0·000	0·0	100·0

point composition diagrams of the optically active enantiomorphs and their racemic modifications have enabled us to determine the nature of the racemic form. Camphoric acid was shown to be a true *dl*-compound. Further the shapes of the curves are similar in the freezing point-composition and solubility-composition diagrams. It may, however, be remarked that whereas the composition of the eutectic point of the melting point-composition curve

is 20 dl : 80 d, that of the invariant point of the solubility-composition curve
at 35° C. is 6 dl : 94 d Just as a comparative idea of the stability of the
racemic camphoric acid can be gathered from the melting point-composition
diagram, so likewise is it evident from the solubility-composition isotherms
(Figs. 1 and 2).   In each of these cases the middle portion forms the greater
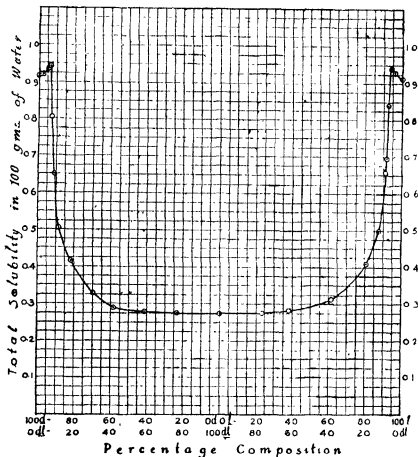
FIG 1

part of the diagram and rises and falls abruptly It may, therefore, be
inferred that the dl-camphoric acid is very stable and its range of stability is
large both in the fused and dissolved states.

PHYSICAL IDENTITY OF ENANTIOMORPHS

    Special interest attaches to the values of rotatory power and solubilities
of enantiomorphic forms of camphoric acid. It was this pair of optically

active acids, the alleged non-identity of whose physical properties was used by Campbell[16] as an argument against Pasteur's Principle of Molecular Dissymmetry. The results of Campbell as regards optical rotation of camphoric acids were shown by one of us to be erroneous[17] In this paper we have shown that the enantiomorphic forms of camphoric acid possess not only identical solubilities at 35° C. but also the solubility-composition
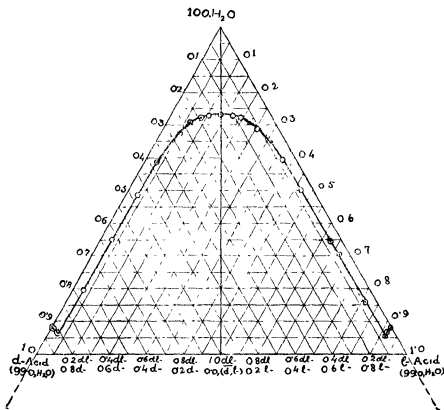
FIG. 2

isotherms of *d*- and *dl*-, and *l*- and *dl*-isomers are exact mirror images of on another (Figs. 1 and 2). This investigation may, therefore, be further adduced as a strong proof of Pasteur's abovementioned principle according to which the *d*- and *l*-forms have physical properties identical in magnitude

SUMMARY

(1) The solubility-composition isotherm for camphoric acids at 35° C. has been determined and shown to consist of three portions indicating the racemic acid to be a true *dl*-compound.

(2) The solubilities of *d*- and *l*-camphoric acids are exactly identical at 35° C.

(3) The shape of the curve enables us to infer that the *dl*-compound is stable and its range of stability is large.

REFERENCES

1	Astbury, W T	*Proc Roy Soc.*, 1923, **104**, 219
2	(a) Centnerzwer	*Zeit Physik Chem*, 1899, **29**, 715
	(b) Adriani	*Ibid*, 1900, A **2**, 462 *et seq.*
	(c) Ross and Somerville	*J C. S*, 1926, 2770
	(d) Singh, B K, and Perti, O N	*Proc Nat Acad Sci. India*, 1943, **13**, 59 1944. **14 A**, 79.
3	Raoult	*Zeit Physik Chem*, 1889. **3**, 372
4	Bruni, *et al*	*Atti R Accad Lincei*, 1902, **11**, 212 , 1904 **5**, 13, 349.
5	Ostwald, W	*Zeit Physik Chem*, 1889. **3**, 372
	Walden, P	*Ber*, 1896, **29**, 1692
6	Marchlewski	*Ibid*, 1892, **25**, 1556
7	Mitchell, A D., and Smith, C.	*J C S*, 1913, **103**, 489
	Smith. C	*Ibid*, 1914, **105**, 1703
8	Stewart, A. W	*Ibid*, 1907, **91**, 1386
9	Singh, B K, *et al*	*Proc Ind Acad Sci*, 1937, **5**, 484
10	Roozeboom, B	*Ber*, 1899, **32**, 537 , *Zeit Physik Chem.*, 1899, **28**, 494
11	Bruni	*Gazetta*, 1900, **30**, 35
12	Bhatia, B B, Singh, B K, *et al*	*Proc Nat Acad Sci India*, 1944, **14**, 171
13	(a) Pasteur, L.	*Alembic Club Reprints*, **14**, 45
	(b) Pratty	*Compt Rend Soc Biol*, 1886, **103**, 137.
	(c) Cushny, A R	*Biological Relations of Optically Isomeric Substances*, London, 1926
	(d) Singh, B K , and Lal, A V	*Nature*, 1939, **144**, 910 , *Proc Ind Acad Sci* 1940, **12 A**, 157, 230
	(e) —— and Prasad, S	*Ibid*, 1936 **3**, 586
14	Singh, B K, and Mahanti, I	*Ibid*, 1935, **2**, 378.
15	Campbell	*J C. S.*, 1930, 179
16	Campbell	*J A C S*, 1931, 1661.
17	Singh, B K.	*Current Science*, 1935, **3**, 420
	—— and Mahanti, I	*Proc Ind Acad. Sci*, 1935. **2**, 378.

THE AZIMUTHAL EFFECT OF COSMIC RAYS AT LAHORE

BY P. S. GILL

(Forman Christian College, Lahore)

THE theory of the motion of charged particles in the earth's magnetic field in its application to cosmic-ray particles was worked out by Lemaitre and Vallarta.[1] One aspect of this theory leads to the study of the azimuthal variation of cosmic-ray intensity, special cases of which are the East-West and North-South asymmetries. Albagli Hutner[2] made a quantitative study of the azimuthal effect of cosmic radiation (variation of cosmic-ray intensity at a given point on the earth's surface and fixed zenith angle but for different azimuths), using a constant zenith angle of 60°, at a geomagnetic latitude of 20° N. This geomagnetic latitude was chosen because the penumbra[3] (the reader is referred to Shremp's paper for reference for details about the penumbra), which makes possible the determination of the energy spectrum of the primary cosmic rays, makes a significant contribution at intermediate latitudes (between 10° and 40° geomagnetic latitude) The author undertook to perform an experiment at Lahore (geomagnetic latitude 22° N.) to find the predicted azimuthal effect for a fixed zenith angle of 60°. Preliminary reports[4] on the experiment appeared earlier. This report sums up the results of the three separate runs of the experiment. The resolving power of the telescope was increased in each successive run.

In the first two runs four cosmic-ray telescopes were used, each consisting of three triple coincidence G-M counter tubes with lead filter of 10·2 cm. while in the third run of the experiment only two telescopes were used. The solid angle range covered in the first, second and third runs were 14 5°, 8·07° and 7·15° in the vertical and 65°, 38·87° and 37 93° in the lateral planes respectively. The telescopes were mounted on the four edges of a square table which was rotated back and forth through an angle of 180°. Interchanging of opposite telescopes, in the first run, was done automatically after an interval of 35 minutes while in the second and the third run the interchanging was done by hand at frequent intervals. The azimuths were changed by steps of 10° each time. During the second run each of the four telescopes swept the whole sky for the fixed zenith angle at intervals of 10° at least twice and

some azimuths were covered more than twice. The two or more readings of one telescope at the same azimuth, though taken about a month and a half apart, do not differ from each other by more than their statistical fluctuations and thus showed the systematic working of the telescope for the whole experimental period. These readings were taken between October 31, 1941 and February 21, 1942.

Compared with the solid angle range of the first run of the experiment that of the second run was reduced giving therefore a resolving power three times as great. The number of counts per unit time for each new telescope should therefore be one-third of the number of counts per unit time in the earlier experiment. The only other difference between the new telescopes and the old was that among the four some of the individual G-M tubes had
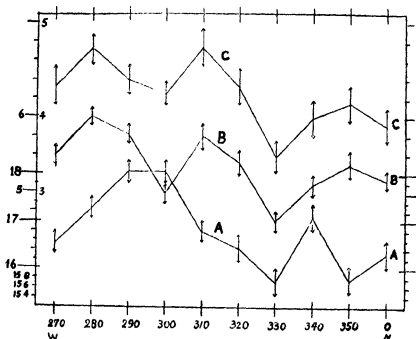
Fig. 1   The azimuthal variations of cosmic-ray intensity for a fixed zenith angle of 60° at Lahore. The vertical scale for each curve is given at the left.

been interchanged. Another rough check on the systematic working of the tubes was provided by the fact that the ratio of the counts per day in the new experiment to that in the old was 1 : 3·12. In the third run the two telescopes covered the azimuths due North-West and South-East directions only. The G-M tubes used in this experiment were of a larger size than those used in the first two runs of the experiment. For the third run the

data presented in this paper, were taken between November 25, 1944 and December 22, 1944.

The apparatus was installed in a special observatory constructed for the purpose on top of the Physics Laboratory of Forman Christian College. The roof of the observatory was made of a single sheet of galvanized iron and was thus virtually open to the sky

Curves of Fig. 1 represent the data of the second run of the experiment. Curves A, B, C. and D of Fig 1 represent the number of triple coincidences per hour obtained by telescopes A, B, C and D for a fixed zenith angle of 60°. Each telescope made a complete turn of the horizon, except for the azimuths where one of the amplifying tubes or one of the power tubes or one of the G-M tubes was not functioning properly. These exceptions are indicated by the gaps in the graphs An examination of these four curves clearly shows the marked irregularities in the North-West quadrant. The humps in the curves in this quadrant occur at the same angles in each curve. No such marked variations at consistent azimuth angles are shown in other quadrants.

Curves A and C represent the data collected by opposite telescopes A and C during the same period, and curve E is the mean of A and C. Similarly curve F is the mean of B and D and represents the data collected by two opposite telescopes B and D during the same period In other words each point of curve F represents data taken about forty days after the data taken for the corresponding point of curve E. In taking the means it is assumed that the efficiency of the two opposite telescopes in each case is the same By and large the number of counts at each angle is doubled, and therefore the statistical errors are reduced. It should be noted that in the N-W quadrant all the points of curve F coincide with those of curve E within the probable errors except at 350°. Even for this angle the general form of the curves is the same. The parallelism between curves E and F is clear enough, with the exception of regions between 140°-70° and between 210°-50°.

Curve G is the weighted mean of all the four telescopes. The means of all the ordinates for a complete turn of the horizon of curve A, and similarly of curves B, C and D were taken separately These means were weighted with reference to the mean of all the ordinates of these four curves (A, B, C, D) and it turned out to be the same as that of telescope A. That is, all the points of curves B, C and D were multiplied by the ratio of their respective means to the general mean or that of curve A It is again to be noted that in the N-W quadrant curve G has marked azimuthal irregularities.
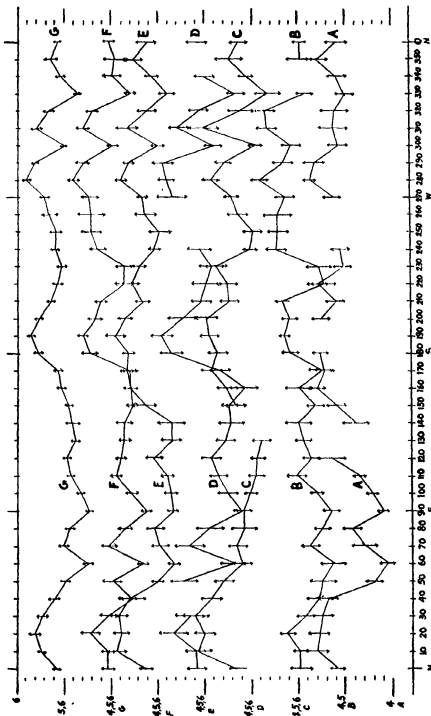
Fig. 2. The azimuthal effect in the N-W quadrant as given by curves A, B, C representing successively decreasing cones subtended by the telescopes.

Two humps, one at 280° and the other at 310° are prominent in this qudrant. The curve in the N-E quadrant varies considerably less. This is in agreement with Hutner's conclusion that in the northern hemisphere, the curve between the N and E directions should be less irregular because of the supposed predominance of positive particles.

Curves of Fig. 2 represent the data of all the three runs of the experiment in the N-W qudrant, where the azimuthal irregularities are much more pronounced and where comparison with the theoretically calculated curve is possible. Curves A, B, C of Fig 2 are the results of the 1st, 2nd and 3rd runs of the experiment respectively. For a wider angle of the telescope in the lateral plane the azimuthal effect averages out as is apparent from curve A. With a smaller angle the widths of maxima and minima in the azimuthal curve should be more pronounced. This is exactly the case as is clearly shown in the curves B and C. Even for these two curves the angle of the telescope in the lateral plane is much larger than the widths of the maxima and minima which are no more than 20° The real curve should show far more pronounced maxima and minima and with this in view the resolving power of the telescope is further increased by decreasing the lateral angle of the telescope to near about 15°. The new results will be published later.

The cone of the telescope used for obtaining curve B is slightly larger than that for curve C and the parallelism between these two curves is significant. The maxima and minima occur at the same angles and are more pronounced in curve C than in B as should be expected. Another point to be noted is the lesser prominence of the hump at 280° than that at 310° for the smaller cone (curve C). This would indicate that as the solid angle subtended by the telescope becomes smaller the 280° maxima begins to flatten out and the 310° maxima comes more and more into prominence. For a very small cone the experimental curve seem to approach the theoretically calculated curve of Hutner, giving the maxima at 310° instead of 305°. This difference in the position of the maxima may also be wiped out for still narrower cones if the telescope is directed towards 305°.

Hutner's results refer strictly to primaries before they enter the atmosphere. In the present experiment the secondaries were filtered off by 10·2 cm. of lead and therefore telescopes recorded the passage of hard secondaries presumably having the same direction as the primaries which were responsible for producing them.

The East-West and North-South Asymmetries

Special cases of the azimuthal effect are the E-W and N-S asymmetries, Tables I and II give the experimental results on these asymmetries at Lahore

TABLE I

Counts per minute in N-W quadrant (N_A) and in the S-E quadrant (N_B)

Angle	N_A	Angle	N_B	$\alpha = 2\dfrac{N_A - N_B}{N_A + N_B}$
0	0·272±0·005	180	0·298±0·006	− 0·091±0·027
350	0·263±0·005	170	0·280±0·005	− 0·062±0·026
340	0·285±0·005	160	0·273±0·005	+ 0·043±0·028
330	0·262±0·005	150	0·267±0·005	− 0·019±0·027
320	0·274±0·005	140	0·267±0·005	+ 0·026±0·026
310	0·280±0·004	130	0·290±0·005	− 0·035±0·016
300	0·301±0·004	120	0·278±0·004	+ 0·080±0·020
290	0·301±0·004	110	0·272±0·004	+ 0·101±0·020
280	0·288±0·004	100	0·252±0·004	+ 0·133±0·016
270	0·276±0·004	90	0·256±0·004	+ 0·075±0·016

TABLE II

Counts per hour from N-E-S (x) and from S-W-N (y)

Angle	X	Angle	Y	$\alpha = 2\dfrac{x-y}{x+y}$
0	5·14±0·10	180	5·53±0·12	− 0·073±0·029
10	5·46±0·11	190	5·69±0·12	− 0·041±0·029
20	5·60±0·13	200	5·52±0·12	+ 0·014±0·032
30	5·44±0·13	210	5·26±0·11	+ 0·021±0·032
40	5·12±0·13	220	5·12±0·13	+ 0·013±0·038
50	4·96±0·13	230	5·04±0·13	− 0·016±0·037
60	4·47±0·12	240	5·18±0·12	− 0·147±0·035
70	4·98±0·13	250	5·16±0·16	− 0·035±0·040
80	4·86±0·13	260	5·30±0·20	− 0·087±0·044
90	4·44±0·09	270	5·40±0·12	− 0·195±0·030
100	4·62±0·09	280	5·80±0·09	− 0·226±0·025
110	4·83±0·11	290	5·61±0·11	− 0·149±0·030
120	4·92±0·12	300	4·99±0·10	− 0·014±0·031
130	4·73±0·12	310	5·60±0·14	− 0·167±0·035
140	4·81±0·18	320	5·32±0·14	− 0·100±0·045
150	4·89±0·11	330	4·70±0·11	+ 0·040±0·032
160	5·05±0·13	340	5·08±0·12	− 0·006±0·035
170	5·10±0·12	350	5·29±0·16	− 0·037±0·038

(geomagnetic latitude 22° north) for a fixed zenith angle of 60°. Table I is the same as Table I already published[4] except for the probable errors, which were not correctly calculated A correction for these errors was sent but due to the present conditions causing delays in mails, the author has not seen it published. Table II gives the results of the 2nd run of the experiment. (x) represents the counts per hour for each angle from N-E-S while (y) gives the counts per hour from S-W-N. The asymmetry $\alpha \simeq 2\dfrac{x-y}{x+y}$ is calculated at each 10° interval.

A notable feature of these asymmetries is that the maximum E-W difference does not coincide with the magnetic E-W plane, but is found to occur in the 280°-100° plane. Each of the four telescopes gives the maximum E-W difference at the same angle (280°-100°). This becomes more significant when we look at Table I, which also shows that the maximum E-W difference occurs in 280°-100° plane.

SUMMARY

Four triple coincidence cosmic-ray telescopes directed at a common zenith angle of 60° were mounted on a turn table. Each telescope represented a vertical plane 90° from that of its neighbour. In each was inserted 10·2 cm. of lead. By 180° reversals each telescope was interchanged in its position with the one directly opposite. Countings were made at settings of the table for every 10 degree of azimuth angle. Azimuthal variations in the North-West and North-East quadrants check qualitatively those theoretically predicted by Hutner. The data are still not sufficient to warrant quantitative comparison. It has been found that the maximum East-West asymmetry does not coincide with the magnetic East-West plane, but occurs at 280°-100° plane.

REFERENCES

1.	G Lemaitre and M S Vallarta	*Phys Rev* 1933, **43**, 88
2.	R. A. Hutner	*Ibid* 1939, **55**, 614
3	E J Shrimp	*Ibid*, 1938, **54**, 157.
4	P S Gill	*Ibid*, 1941, **60**, 153; *Proc Nat Inst of Sciences, India*, 1943, No 2, 251-52

INTENSITY VARIATIONS IN THE FIRST POSITIVE AND SECOND POSITIVE BANDS OF NITROGEN EXCITED BY HIGH FREQUENCY OSCILLATIONS

BY R. K. ASUNDI AND JAGDEO SINGH*

(Department of Physics, Benares Hindu University)

INTRODUCTION

HIGH frequency oscillations have been used by many workers for the excitation of the spectra of atoms and molecules. Hulburt[1], before the theory of molecular spectra had developed, investigated the spectra of hydrogen, oxygen and air in the spectral region 3500–5000 Å, by exciting the gases by discharges of various frequencies, viz, 60, 3×10^5, 10^6 and 0.43×10^7 cycles per second. The spectra were reported to be unmodified by the changes in frequency. In the case of hydrogen, the Balmer lines were faint and the spectrum consisted mainly of about 300 lines of the secondary spectrum and a faint continuum. Later, however, Brasefield[2] obtained some striking results in his investigations on the spectrum of hydrogen excited by h.f. discharge. These were followed by a study of the excitation functions of the lines of molecular hydrogen.[3] For this purpose, the optical densities of the lines were measured under excitation by electron impact and plotted against the exciting voltages. In this way, Brasefield investigated a large number of lines of the $np^3\Pi \rightarrow 2\ s^3\Sigma$ systems and compared them with typical lines of the singlet systems. In each case a sharp distinction between the excitation function of the lines of singlet and triplet systems was found, the singlets being relatively more enhanced at electron energies much higher than the excitation potential while the triplets are strongest at energies very close to it. In this respect, the difference in the excitation functions is quite similar to that between the corresponding excitation functions for the mercury atom. Further work on hydrogen bands excited by h.f. discharge enabled Brasefield[4,5] to correlate the frequency of discharge and its equivalent electron velocity and offer a simplified mechanism of h.f. discharge. He finds that his experimental results can be fully explained under the following assumptions:—

   1. The electron velocities increase as the voltage between the electrodes is increased, the gas pressure and the frequency of oscillations being kept constant.

---

* At present Lecturer in Physics, Udai Pratap College, Benares.

2. For a given voltage between the electrodes, the electron velocity is greater the smaller the frequency of oscillations.

3. The electron velocity decreases as the pressure of the gas is increased.

It is to be remembered, however, that for the above assumptions to have theoretical justification, the main process of excitation should involve the emitters in the normal state only.

Similar results are obtained in the excitation by h f. oscillations of the atomic spectrum of mercury.[6,7] In this case, however, a more recent investigation[8] indicates that the mechanism of excitation becomes complicated at higher pressures at which, therefore, the simple relation between the relative intensities of the singlet and triplet lines breaks down Many other similar changes in intensity distribution in spectra excited by h f. discharge have been observed in this laboratory and briefly reported.[9,10,11] Working with a discharge tube containing a trace of air, it was observed that the colour of the discharge underwent a remarkable change when the frequency of the exciting oscillations was changed. The glow which was pinkish red at lower frequencies gave place to an orange yellow colour when the frequency of oscillations was increased. The change over from one colour to the other took place rather sharply at a frequency of exciting oscillations of 735*, below and above which it was red and yellow respectively. These variations have been studied spectroscopically in the visible region where the spectrum of the glow consists of the first positive and second positive band systems of nitrogen. A few suitable bands belonging to the first positive system and some to the second positive system were selected for a study of relative intensity changes depending upon the frequency of exciting oscillations. The results obtained are presented in this paper.

EXPERIMENTAL

In these experiments a glass discharge tube of the π type was used. It was about 20 cm. long and 1 cm in diameter. Two bulbs containing P_2O_5 and crushed KOH were also sealed on to it. The discharge tube had internal electrodes of aluminium in its two vertical limbs These however, were not used and the excitation was brought about by two external electrodes of tin foil wrapped round the horizontal part of the discharge tube and separated from each other by a distance of about 5 cm. The tube was provided with a quartz window which was attached to one of its ends by sealing wax. This, however, was not very necessary because there was no suitable spectro-

---

* Frequencies are expressed in kilo-cycles per second.

A2

graph available which would photograph the visible and the ultra-violet regions of the spectrum with sufficient dispersion on one plate.

The source of h.f. oscillations was a modified Hartley circuit containing a Phillips triode valve T C 04|10 D 17 taking a filament current of 1 amp. and an anode potential of 340 volts. The frequencies of oscillations obtained varied between 600 and 1500 depending upon the variable condenser readings which were calibrated in terms of frequencies by means of an absorption frequency meter. The discharge tube was sealed onto an evacuating apparatus consisting of a high vacpump, a mercury manometer and a number of bulbs containing P_2O_5, KOH and $CaCl_2$. The tube was thoroughly evacuated and freed from impurities of carbon after which a small amount of air was introduced by an artificial leak. The pressure in the tube was again adjusted by running the pump and when the discharge could be easily passed using the external electrodes, the tube was sealed off from the evacuating apparatus. The resolving instrument used was a Hilger constant deviation glass spectrograph. The discharge tube was set in proper collimation with the spectrograph and the light from the discharge tube was focussed by a lens onto the slit of the spectrograph. During each series of exposures, except for the lowering of the plate holder, no other part of the arrangement was touched, so that the collimation and the focussing lens were strictly undisturbed throughout the series of exposures. Ilford H.P 2 (hypersensitive panchromatic) plates were used. An exposure time of 5 minutes was found suitable. Since the nitrogen bands could be easily identified by reference to a previously measured plate taken on the same setting of the spectrograph, no standard lines were found necessary and hence were not taken on the spectra.

Fig. 1 is typical of the plates obtained. It contains 14 spectra excited by various frequencies of oscillations which are marked on the plate. The last two exposures 13 and 14 differ only in the matter of time of exposure which for 14 is one minute. For all other exposures the exposure time is 5 m. The groups of first positive and second positive bands are indicated in Fig 1. From this spectrogram exposures 5, 6, 7 and 12 were selected for a microphotometric study. They were run under a Zeiss recording microphotometer* and the four curves obtained are given in Figs. 2, 3, 4 and 5 which represent the exposure numbers 5, 6, 7 and 12 respectively. Of the first positive bands three at 5371, 5406, 5441 Å and of the second positive seven bands at 4355, 4417, 4490, 4649, 4724, 4815 and 4916 Å were chosen for study and these are indicated in Figs 1 and 4.

From the microphotograms, the following values are calculated:—
I_0, the distance between the limits of clear background and complete darkness and I, the distance between the maximum of the peak and the limit of complete darkness (see Fig. 3). In cases where the fine structure of the preceding band is superposed on the band head, the blackening due to the superposed fine structure is taken into account in arriving at the true I value for the band head. In this way values of the optical density S are evaluated as $\log_{10}$ I_0/I, for the three first positive and the seven second positive nitrogen bands in the four selected exposures and are given in Table I.

TABLE I

Optical Densities

Exp No	2nd positive bands at A							1st positive bands at A			Excitation Frequency
	4355	4417	4490	4649	4724	4815	4917	5371	5406	5441	
5	·33	·13	·24	14	·13	·16	·11	·15	·17	·17	680
6	·28	·10	·29	·11	·11	·11	·09	·15	·15	·17	695
7	·28	·21	20	·18	19	13	·12	32	·32	32	715
12	·13	·10	·18	14	·07	·07	·08	·37	·36	·36	790

DISCUSSION

From the four curves it will be seen that for all the selected bands the density of blackening is neither very low nor has it reached the saturation limit. We are thus working on the straight line portion of the characteristic curves connecting the density and intensity for the photographic plate. In any case, if the wavelength of the radiation affecting the plate is also kept constant, that is to say, if we compare the density of the same band at various frequencies of excitation, since other factors (time of exposure, age and nature of plate, its subsequent treatment in developing, etc.) which govern the density are kept strictly the same, a change in density always means a corresponding change in intensity even though the converse may not hold (*e.g.*, very low intensity or saturation limit).

Table I shows that the intensity of every single second positive band in general shows an increase at the three frequencies 715, 695 and 680 over its value at frequency 790. On the other hand, the reverse is true for every single first positive band. The average intensity of the first positive bands at frequency 790 is represented by S = ·36. This reduces to ·32 at frequency 715 and to ·16 at frequencies 695 and 680. Thus the optical density of the bands is reduced to about half its value. On

the other hand, for the second positive bands the average value of S for frequency 790 is ·11 and this increases to 19 at frequencies 715 and 680. There is a slight drop in density at frequency 695 but even then the value is greater than that at 790   We can thus conclude that the three bands of the first positive system decrease in intensity as the frequency of exciting oscillations is reduced from 790 to 680 while the seven bands of the second positive system exhibit exactly the opposite behaviour. The process of excitation being essentially one of electronic impact one would expect that similar effects will be exhibited by the rest of the bands of the two systems.

In this connection the experiments of Brasefield on the controlled excitation by electronic impact of molecular hydrogen and h f. discharge in hydrogen are particularly informative. It will be quite interesting to see if his assumptions can help us to understand the changes in intensity observed In the energy level diagram of nitrogen bands, the second positive system involves the transition $C^3\Pi_u \to B^3\Pi_g$ Its excitation potential which is represented by the position of the $C^3\Pi_u$ level is 10·98 e.v. Similarly the first positive bands arise out of the transition $B^3\Pi_g \to A^3\Sigma_u{}^+$ and have an excitation potential of 7 32 e v. which represents the position of the $B^3\Pi_g$ level.[12] If we make the plausible assumption that in the present experiments the changes in frequency do not bring about changes in the voltage across the electrodes to an appreciable extent then according to the assumption 2 of Brasefield, the second positive bands should be stronger at lower than at higher frequencies because then the equivalent e.v. will be the greater. Similarly the first positive bands should be stronger at higher frequencies than at lower ones. This is exactly what is observed.

But the fact that there is a frequency below which the glow is pinkish red and above which it is orange yellow still remains to be explained. This change in colour is presumably connected with the relative intensities of the two band systems Such a behaviour strongly suggests that here we are concerned with a well-known phenomenon observed in experiments on the controlled excitation of spectra, we mean the dependence of excitation function of an energy level of atoms or molecules on the velocity of the colliding electron, reference to which we have already made. For such experiments it is of course necessary that all the emitters must be excited from the normal state, so that indirect excitation be negligible. The phenomenon is particularly striking for even electron-emitters which give rise to singlet and triplet electronic states. In the present case, however, we are concerned not with a singlet and a triplet state but with two systems each of which is a triplet. The excitation functions of some of the bands of the second positive system

have been investigated by Langstroth.[13] All the three bands investigated show that their excitation function is that typical of the triplet states. Though the intensity of the maxima for the three bands is not the same it may be noted that the position of the maximum is nearly the same namely about 17 e.v. The excitation function of the first positive bands has been investigated by Bernard and Fouilloure.[14] In this case also the nature of the curve is the same, but the maximum intensity occurs for a velocity of 13·5 e.v. of the colliding electrons. Since the two curves, the one typical of the second positive bands and the other typical of the first positive bands, will intersect each other at a point for which the velocity of the electrons will be about 15 e.v., this will be the transition electron velocity below which the first positive bands will be stronger than the second positive bands and above which the reverse will be true. The colour changes observed in the present experiments therefore indicate that this transiton velocity for electrons is reached when the frequency of exciting oscillations is about 735. The fact that such a correlation is at all possible further indicates that in the present experiments the excitation involves molecules from their normal state.

SUMMARY

    A discharge tube containing air at low pressure is excited by h.f. frequency oscillations from a modified Hartley circuit. It is observed that there is a critical frequency of exciting oscillations, namely 735 k c./sec. below which the colour of the discharge is pinkish red and above which the colour is orange yellow. The spectrum of the discharge in the visible region consists of the first positive and second positive bands of nitrogen. A study of some of these bands as regards their intensity variation depending upon the frequency of exciting oscillations is made. It is found that the first positive bands at 5371, 5406 and 5441 Å decrease in intensity as the frequency of exciting oscillations is reduced from 790 to 680 k.c./sec. The second positive bands at 4355, 4417, 4490, 4649, 4724, 4815 and 4917 Å on the other hand, increase in intensity under the same conditions. The results are in harmony with the theoretical conceptions, regarding such phenomena and allow us to conclude that in the present experiments an energy of 15 e v. is available for excitation when oscillations of frequency 735 k c./sec. are used.

REFERENCES

1   E. O. Hulburt   *Phys Rev*, 1922, **20**, 127.
2   C J Brescheld   *Ibid*, 1929, **33**, 925
3   ——————————   *Ibid*, 1929, **34**, 431
4   ——————————   .   *Ibid*, 1930, **35**, 92 and 122
5   ——————————   *Ibid*, 1930, **35**, 1073.
6   S Tolansky   *Proc Phys Soc London*, 1930, **42**, 556 , 1931, **43**, 545
7   D D Pant   *M Sc Thesis*, Benares Hindu University, 1942
8   N L Singh   *D Sc Thesis*, Benares Hindu University, 1944
9   R K Asundi, N L. Singh   *Proc Ind Sci Cong*, 1942, 3, 35.
    and J Singh
10 ——————, ———— and D D   *Ibid*, 1942, 3, 35
    Pant
11 ———— and N L Singh   *Nature*, 1942, **150**, 123
12 H Sponer   *Molekuel Spektren*, 1935
13. G O Langstroth   *Proc Roy Soc London*, 1935, **150 A**, 71
14. R Barnard and R. Foulloure   *Comp. Rend*, 1939, **209**, 647.

R. K. Asundi and
Jagdeo Singh

Proc. Ind. Acad. Sci. A, vol XXII, Pt I

Exp. No   ←2nd Positive N₂ bands   ←1st Positive N₂ bands   Excitation frequency

FIG. 1

FIG. 2

R. K. Asundi and
Jagdeo Singh

Proc. Ind. Acad. Sci., A, vol. XXII, Pl. II

For Peak
4355
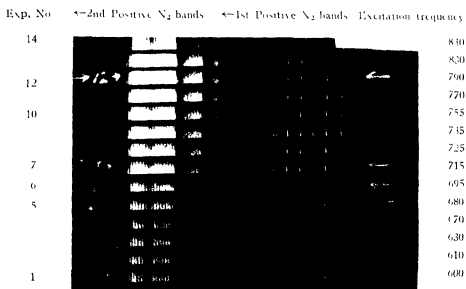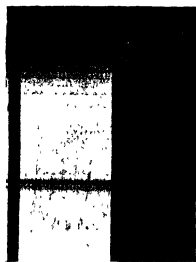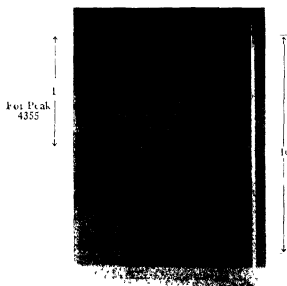
FIG. 3

2nd positive Peaks   1 1 positive Peaks
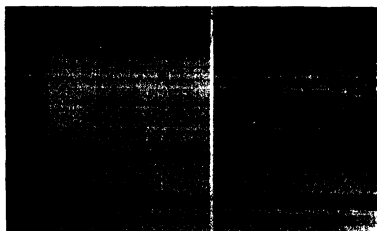
FIG. 5   FIG. 4

ON DIFFUSER EFFICIENCY IN COMPRESSIBLE FLOW

BY P. NILAKANTAN

INTRODUCTION

THE diffuser is a device whereby the kinetic energy of flow of a high velocity fluid jet is transformed into pressure energy It has many practical applications in turbines, wind tunnels, pumps and various duct systems.

The conditions of fluid flow in the diffuser are determined by the energy equation and the equation of continuity of fluid dynamics In the simple case of the flow of an incompressible fluid, or the case of a compressible fluid at very low Mach numbers, these equations are:

$$P_1 U_1 A_1 + \tfrac{1}{2}\rho U_1{}^3 A_1 = P_2 U_2{}^3 A_2 + \tfrac{1}{2}\rho U_2{}^3 A_2 \tag{1}$$

$$U_1 A_1 = U_2 A_2, \tag{2}$$

where P_1, U_1, A_1 and P_2, U_2, A_2 denote the pressure, velocity and area of cross-section at the entrance and exit sections of the diffuser, respectively, and ρ is the density of the fluid. The efficiency of the diffuser is defined as the fraction of the difference in the kinetic energy of the jet at the entrance and exit sections that is transformed into pressure energy, that is,

$$\eta = \frac{P_2 U_2 A_2 - P_1 U_1 A_1}{\tfrac{1}{2}\rho U_1{}^3 A_1 - \tfrac{1}{2}\rho U_2{}^3 A_2} \,\, \overset{\cdots}{=} \frac{P_2 - P_1}{\tfrac{1}{2}PU_1{}^2 - \tfrac{1}{2}PU_2{}^2} = \frac{P_2 - P_1}{q_1 - q_2}. \tag{3}$$

Another definition of diffuser efficiency used in design expresses it as the ratio of the difference of pressure between the entrance and exit sections to the dynamic pressure at the entrance, that is,

$$\eta = \frac{P_2 - P_1}{P_0 - P_1} = \frac{P_2 - P_1}{q_1}. \tag{4}$$

where P_1 and P_2 are the pressures at the entrance and exit respectively and P_0 is the stagnation pressure. This quantity, however, does not give any indication of the energy losses involved. On the other hand, the efficiency as defined by (3) does not give the fraction of the kinetic energy at the entrance that is actually transformed into pressure. Hence both definitions are useful when designing a diffuser in order to obtain maximum pressure recovery with a minimum energy loss. Formulæ (3) and (4) are directly applicable only under ideal flow conditions. And in view of the fact that under actual conditions the velocity of the jet is not constant across any section

of the diffuser, the definition of efficiency according to equation (3) has to be suitably modified in order that it may be calculated from actual experimental data. We shall assume that the static pressure and the density are constant across any section, which is justifiable when the divergence angle of the diffuser is small. In this case, we get the following expression.[1]

$$\eta = \frac{P_2 - P_1}{\frac{1}{2}\rho \bar{U}_1{}^2 \left\{\alpha - \beta \left(\frac{A_1}{A_2}\right)^2\right\}} \qquad (5)$$

where,

$$\int_{A_1} \frac{1}{2}\rho U^3 dA = \frac{1}{2}\rho \bar{U}_1{}^3 A_1 \alpha$$

$$\int_{A_2} \frac{1}{2}\rho U^3 dA = \frac{1}{2}\rho \bar{U}_2{}^3 A_2 \beta$$

A_1 and A_2 are the entrance and exit areas of cross-section as defined before and $\bar{U}_1$ and $\bar{U}_2$ are the average velocities respectively, defined by the relations,

$$\bar{U}_1 = \frac{\int_{A_1} U dA}{A_1} \qquad (6)$$

$$\bar{U}_2 = \frac{\int_{A_2} U dA}{A_2} .$$

Hence the determination of the efficiency at low speeds involves the measurement of P_1, P_2, U_1 and U_2 and the calculation of $\bar{U}_1$, $\bar{U}_2$, α and β under conditions of steady flow.

At high speeds, when compressibility effects become prominent, the above definitions of the diffuser efficiency are no longer sufficient and we run into thermodynamic complications. The object of the present paper is to present a practical solution of the problem in the case of compressible flow that has been employed by the author in testing scale models of several diffusers for a high speed wind-tunnel.

THEORETICAL CONSIDERATIONS

Ackeret[2] has defined diffuser efficiency in compressible flow as

$$\eta = \frac{P_2 - P_1}{P_0 - P_1} \qquad (7)$$

which is the same as formula (4) in the case of incompressible fluid flow. But η is not equal to $\frac{P_2 - P_1}{q_1}$ since, in compressible flow,

$$(P_0 - P_1) = q_1 \left(1 + \frac{1}{4} M_1{}^2 + \frac{1}{40} M_1{}^4 \dots\right)$$

We may therefore write $\eta = \dfrac{P_2 - P_1}{q_1 \left(1 + \frac{1}{4} M_1^2\right)}$, to a first approximation. The efficiency as defined above does not again give any indication of the energy losses. A satisfactory definition in the case of compressible fluid flow has been used by L. Crocco[8] in his important paper on high speed wind-tunnels, taking into consideration the non-isentropic character of the flow. According to the Bernoulli equation for the flow of a non-viscous compressible fluid, we have the following fundamental relation :

$$U dU = -\frac{dP}{\rho} \tag{8}$$

L. Crocco assumes that the actual equation of flow, taking into account frictional dissipation of heat, is of the form,

$$\eta U dU = -\frac{dP}{\rho} \tag{9}$$

where η is the efficiency factor.

The problem of determining η reduces to that of integrating the above expression. If in the first place, η is assumed to be constant for any flow under specified conditions in the diffuser, then,

$$\eta \frac{(U_1^2 - U_2^2)}{2} = -\int_{P_1}^{P_2} \frac{dP}{\rho}. \tag{10}$$

Due to the frictional evolution of heat during the transformation, the changes taking place are no longer isentropic and in order to integrate $\dfrac{dP}{\rho}$, it will be necessary to know the actual law governing the variation of P with ρ. This law will be different from the usual adiabatic relation, $\dfrac{P}{\rho^\gamma} =$ constant, although of the same form. It may be noticed that in equation (10), η is the fraction of the kinetic energy which is transformed into pressure energy and hence is the efficiency of the diffuser while $(1 - \eta)$ is the fraction of the energy which is rendered unavailable from the standpoint of pressure recovery.

The definition of the equation of flow expressed by (9), which is characteristic of the diffuser, defines also the adiabatic non-isentropic law of variation of pressure with density, if we regard η as a constant for the diffuser under any specified condition of velocity and pressure distribution. In this connection it must be clearly borne in mind that η is not a constant for the diffuser *under all conditions of flow*. In other words, if we specify any condition of fluid by the Mach number at the entrance of the diffuser,

A3

then η will be a function of this Mach number   Corresponding to each Mach number, we shall have a certain velocity distribution across the entrance and exit sections of the diffuser, a corresponding pressure distribution along the length of the diffuser, and a certain value of η (regarded as constant only for the flow from the entrance of the diffuser to its exit) which we shall now express in terms of the other quantities.   This can be accomplished with the help of the energy equation,

$$d\left(\frac{U^2}{2}\right) + Jdi = 0,\qquad(11)$$

where di is equal to $C_p\, dT$ and J is the mechanical equivalent of heat.

Hence, $$J\, d_i = \frac{1}{\eta}\frac{dP}{\rho} = J\, C_p\, dT = \frac{\gamma}{(\gamma - 1)}R dT,\qquad(12)$$

where γ is the ratio of specific heats and R is the gas constant defined by the relation $P/\rho = RT$. Equation (12) may then be reduced to the form,

$$\frac{dP}{P} = \frac{\gamma\eta}{(\gamma - 1)}\frac{dT}{T}\qquad(13)$$

which gives an integration,

$$\log P = \frac{\gamma\eta}{(\gamma - 1)}\log T + C\qquad(14)$$

i e , $\dfrac{P}{T^{\left(\frac{\gamma\eta}{\gamma - 1}\right)}}$ is constant.

From the equation of state we also get the relation connecting pressure and density as follows

$$\frac{P_1}{P_2} = \left(\frac{\rho_1}{\rho_2}\right)^{\frac{\gamma\eta}{(\gamma\eta - \gamma + 1)}}\qquad(15)$$

The above relation enables us to integrate equation (10) and we get,

$$\tfrac{1}{2}(U_1{}^2 - U_2{}^2) = \frac{\gamma}{\gamma - 1}RT_1\left\{\left(\frac{P_2}{P_1}\right)^{\frac{(\gamma - 1)}{\gamma\eta}} - 1\right\}.\qquad(16)$$

The subscripts 1 and 2 refer to the entrance and the exit of the diffuser respectively.

The following special case of equation (16) is interesting. If U_2 approaches zero, P_2 becomes, in the limit, the stagnation pressure at the exit, and we have,

$$\tfrac{1}{2}U_1{}^2 = \frac{\gamma}{(\gamma - 1)} - RT_1\left\{\left(\frac{P_2}{P_1}\right)^{\frac{(\gamma - 1)}{\gamma\eta}} - 1\right.\qquad(17)$$

Dropping the subscript 1 and designating the exit pressure as P_0, the equation becomes,

$$\frac{1}{2} \frac{U^2}{a^2} = \frac{1}{(\gamma - 1)} \left\{ \left(\frac{P_2}{P_1} \right)^{\frac{(\gamma - 1)}{\gamma \eta}} - 1 \right\} \tag{18}$$

where a is the local velocity of sound: $a = \sqrt{\frac{\gamma P}{\rho}}$.

Hence,

$$\frac{P_0}{P} = \left\{ 1 + \frac{(\gamma - 1)}{2} \frac{U^2}{a^2} \right\}^{\frac{\gamma \eta}{(\gamma - 1)}} \tag{19}$$

The corresponding formula for the isentropic case given by Glauert[4] is,

$$\frac{P_0}{P} = \left\{ 1 + \frac{(\gamma - 1)}{2} \frac{U^2}{a^2} \right\}^{\frac{\gamma - 1}{\gamma}} \tag{20}$$

Equation (16) is still not in a suitable form for making any computations from experimental data, since the velocity distribution is not uniform across the entrance and exit sections

If $\bar{U}_1$ and $\bar{U}_2$ are the average velocities, then by the continuity condition,

$$A_1 \bar{U}_1 \rho_1 = A_2 \bar{U}_2 \rho_2. \tag{21}$$

We shall make the simplifying assumption that P_1, P_2, ρ_1 and ρ_2 are constant across any section of the diffuser. Further, we shall define,

$$\int_{A_1} U^2 dA = \alpha \bar{U}_1^2 A_1,$$

$$\int_{A_2} U^2 dA = \beta \bar{U}_2^2 A_2,$$

Also,

$$\bar{U}_2^2 = \left(\frac{A_1}{A_2} \right)^2 \left(\frac{\rho_1}{\rho_2} \right)^2 \bar{U}_1^2 \text{ from } (21).$$

Then equation (16) becomes,

$$\frac{1}{2} \left\{ \alpha \bar{U}_1^2 - \beta \left(\frac{A_1}{A_2} \right)^2 \left(\frac{\rho_1}{\rho_2} \right)^2 \bar{U}_1^2 \right\} = \frac{\gamma}{\gamma - 1} \frac{P_1}{\rho_1} \left\{ \left(\frac{P_2}{P_1} \right)^F - 1 \right\} \tag{22}$$

where

$$F = \frac{\gamma - 1}{\gamma \eta}.$$

If further, it is assumed that the velocity is constant across the entrance of the diffuser (which is generally the case) so that $\alpha = 1$, we have,

$$1 - \beta \left(\frac{A_1}{A_2} \right)^2 \left(\frac{P_1}{P_2} \right)^{2(1-F)} = \frac{\gamma}{(\gamma - 1)} \frac{P_1}{q_1} \left\{ \left(\frac{P_2}{P_1} \right)^F - 1 \right\} \tag{23}$$

since

$$\left(\frac{P_1}{P_2} \right)^{1-F} = \frac{\rho_2}{\rho_1}.$$

·Hence

$$1 + \frac{\gamma}{(\gamma-1)}\frac{P_1}{q_1} = \beta \left(\frac{A_1}{A_2}\right)^2 \left(\frac{P_1}{P_2}\right)^{2\,(1-F)} + \frac{\gamma}{(\gamma-1)}\frac{P_1}{q_1}\left(\frac{P_1}{P_2}\right)^{-F}. \quad (24)$$

We have to solve the above equation for F.

Putting

$$\frac{\gamma}{(\gamma-1)}\frac{P_1}{q_1} = R, \text{ and } \left(\frac{P_1}{P_2}\right)^{-F} = S$$

we have,

$$1 + R = \beta \left(\frac{A_1}{A_2}\right)^2 \left(\frac{P_1}{P_2}\right)^2 S^2 + RS, \quad (25)$$

which is a quadratic in S and gives as a solution

$$S = \frac{-R + \sqrt{R^2 + 4\beta\,(1+R)\left(\frac{A_1}{A_2}\right)^2\left(\frac{P_1}{P_2}\right)^2}}{2\beta\left(\frac{A_1}{A_2}\right)^2\left(\frac{P_1}{P_2}\right)^2}$$

taking only the positive value of S.

Then,

$$\log S = -F \log \left(\frac{P_1}{P_2}\right)$$

i.e.,

$$F = \frac{\log S}{\log \left(\frac{P_2}{P_1}\right)} \quad (26)$$

∴

$$\eta = \frac{(\gamma-1)}{\gamma} \frac{\log \left(\frac{P_2}{P_1}\right)}{\log S}. \quad (27)$$

OUTLINE OF EXPERIMENTAL AND COMPUTATIONAL PROCEDURE

The quantities that have to be determined experimentally are P_1, P_2, q_1 and β P_1, P_2 and q_1 may be easily determined by means of a suitable Pitot-static tube, whereas the determination of β will involve the evaluation of $\int_{A_1} U^2 dA/\bar{U}_2^2 A_2$, as defined earlier. This involves a velocity survey of the exit section for the integration of $U^2 dA$ The value of U at various points on the exit section may be determined by pitot traverses across the section, reasonably sufficient to cover the whole area and to take into account all variations of velocity. $\bar{U}_2$ is given by the relation $\frac{\int_{A_1} U dA}{A_2}$ and may also be evaluated from the velocity survey.

The steps in the calculation of η from the experimental data obtained are as follows:

(1) Calculate $R = \frac{\gamma}{\gamma-1}\frac{P_1}{q_1}$

(2) Evaluate $\bar{U}_2 = \dfrac{\int_{A_2} U dA}{A_2}$

and $\beta = \dfrac{\int_{A_2} U^2 dA}{\bar{U}_2{}^2 A_2}$ from the velocity survey at the exit section.

(3) Calculate $S = \dfrac{-R + \sqrt{R^2 + 4\beta(1+R)\left(\frac{A_1}{A_2}\right)^2\left(\frac{P_1}{P_2}\right)^2}}{2\beta\left(\frac{A_1}{A_2}\right)\left(\frac{P_1}{P_2}\right)^2}\,\lambda$, and

finally find $\eta = \dfrac{(\gamma - 1)}{\gamma}\dfrac{\log\left(\frac{P_2}{P_1}\right)}{\log S}$.

DISCUSSION

No attempt will be made here to discuss the results of earlier experimental work on diffuser efficiency at comparatively low speeds. Regarding these, reference may be made to the article by G N Patterson, on modern diffuser design[1] and also to the article on turbulent flow by H. Bateman[2] in which he discusses flow in a conical channel Published data on the efficiency of high speed diffusers are unfortunately meagre since the subject has come into prominence only recently. The formulæ for efficiency presented in this paper are expected to be useful in future experimental work.

It may be remarked that theoretical formulæ for estimating losses in any new design of a diffuser are of little practical value. Empirical formulæ based on previous experimental work may be of limited use. It has been established that at low speeds a conical diffuser of about 7 degrees divergence angle is about the most satisfactory one High speed jets, however, exhibit a tendency to separation for divergence angles even as low as 5 degrees. The character of the divergence of the cross-section from the entrance to the exit also appears to be a critical factor. Straight walls are more satisfactory than curved walls and, contrary to conventional ideas based on experiments at low speeds, greater efficiency is achieved by designing for a rapid expansion at the entrance followed by a slower expansion rate near the exit than *vice versa*. In any case the design of a high speed diffuser to meet specified conditions remains at present, a problem that can be solved satisfactorily only after considerable experimentation. Accumulation of a vast amount of data will no doubt provide theoretical bases for future design

SUMMARY

An expression for diffuser efficiency in compressible flow has been developed. Experimental procedures for the determination of the efficiency are outlined and the steps for calculating it from the experimental data are indicated.

REFERENCES

1	Parkinson		"Modern Diffuser Design," *Aircraft Engineering*, 1938, **10**, 267
2	Ackeret	.	"High Speed Wind Tunnels," *N A C A Tech Memo*, 1936, No. 808.
3	Croco		*Atti dell' Associazione Italiana di Aerotecnica*, 1939-40, **19.**
4.	Glauert		*Aerofoil and Airscrew Theory*, Cambridge University Press, 1926
5	Bateman		*Bulletin of the National Research Council*, Washington, D C., 1931, No. 84, 469.

THE USE OF GENERALISED DIRICHLET'S INTEGRAL IN SOLVING SOME DISTRIBUTION PROBLEMS OF STATISTICS*

BY P. V. KRISHNA IYER

(Imperial Agricultural Research Institute, New Delhi)

Received November 25, 1943

(Communicated by Rao Bahadur B Viswa Nath, F A Sc)

1. INTRODUCTION

THE distribution of the mean, the standard deviation and other statistical constants of a sample drawn from a known population can be derived by various methods. Of these mention may be made of the geometrical methods due to Professor Fisher by the aid of which some of the distributions of certain statistical estimates in the case of normal populations can be determined very easily. It is also known that the use of the characteristic and moment generating functions enables us to get the distribution of estimates of *statistics* of samples belonging to normal and other populations. This has been applied in a number of cases by Irwin, Kullback and Wishart and Barttlet and others. The purpose of the present paper is to show how the generalised Dirichlet's integral enables us to evaluate the distribution of certain statistical constants of samples drawn from normal and non-normal populations. Kosambi has used this integral to get the distribution of the ratio of the generalised variances of two samples from a bivariate population.

The integral referred to is the well-known multiple integral

$$\int\int..\int F\left\{\left(\frac{x_1}{a_1}\right)^{p_1}+\left(\frac{x_2}{a_2}\right)^{p_2}..\left(\frac{x_n}{a_n}\right)^{p_n}\right\}x_1^{l_1-1}x_2^{l_2-1}..x_n^{l_n-1}dx_1dx_2..dx_n....$$

$$=\frac{a_1^{l_1}a_2^{l_2}..a_n^{l_n}}{p_1p_2..p_n}\frac{\Gamma\frac{l_1}{p_1}\Gamma\frac{l_2}{p_2}..\Gamma\frac{l_n}{p_n}}{\Gamma\frac{l_1}{p_1}+\frac{l_1}{p_1}..+\frac{l_n}{p_n}}\int_0^W W^{\frac{l_1}{p_1}+\frac{l_2}{p_2}..\frac{l_n}{p_n}-1}F(W)\,dW \quad (1)$$

where $x_1, x_2,..x_n$ extend to all positive values subject to the condition

$$\left(\frac{x_1}{a_1}\right)^{p_1}+\left(\frac{x_2}{a_2}\right)^{p_2}+....\left(\frac{x_n}{a_n}\right)^{p_n}=W, \quad (2)$$

* Part of this paper was read before the 28th Session of the Indian Science Congress held at Benares, January 1941, vide Proceedings, Pt. III, p 11 (2) Throughout this paper *m* and σ^2 stand for the mean and the variance of the population, while *x* and *v* or s^2 denote the mean and the variance of the sample on the basis of the size of the sample

75

It may be noted that it follows from (1) that the chance of W lying between W and W + dW subject to condition (2) is proportional to

$$W^{\frac{l_1}{p_1} + \frac{l_2}{p_2} \cdots \frac{l_n}{p_n} - 1} F(W) \, dW \qquad (3)$$

2 NORMAL POPULATION

The probability that a sample of values $x_1, x_2 \ldots x_n$ should fall within the elementary ranges $dx_1 \, dx_2, \ldots dx_n$ is

$$\frac{1}{(\sqrt{2\pi}\,\sigma)^n} \, \text{Exp.} - \frac{1}{2\sigma^2} \sum_1^n (x_r - m)^2 \cdot dx_1 \, dx_2 \ldots \quad dx_n \qquad (4)$$

Putting $\dfrac{x_1 + x_2 \ldots x_n}{n} = \bar{x}$, expression (4) can be transformed into

$$\frac{n}{(\sqrt{2\pi}\,\sigma)^n} \, \text{Exp.} - \frac{1}{2\sigma^2} \left\{ \sum_1^n (x_r - \bar{x})^2 + n(\bar{x} - m)^2 \right\} dx_1 \, dx_2 \ldots dx_{n-1} \, d\bar{x} \quad (5)$$

Now it can be shown, as has been done by Fisher, that

$$\frac{1}{n} \sum_1^n (x_r - \bar{x})^2 = \frac{1}{n} \sum_1^n \xi_r^2 = v, \text{ where}$$

$$\xi_r = \frac{\sum_1^r x_r - r \, x_{r+1}}{\sqrt{r(r+1)}}$$

$\xi_1, \xi_2 \ldots \xi_{n-1}$ are all independent and orthogonal.

Expression (5) in view of the fact $J = \dfrac{1}{\sqrt{n}}$ reduces to

$$\frac{\sqrt{n}}{(\sqrt{2\pi}\,\sigma)^n} \, \text{Exp.} - \frac{1}{2\sigma^2} \sum_1^{n-1} \xi_r^2 \cdot d\xi_1 \, d\xi_2 \ldots \quad d\xi_{n-1} \cdot \text{Exp.} - \frac{n}{2\sigma^2} (\bar{x} - m)^2 \, d\bar{x}$$

using (1) we find that the chance of V lying between V and V + dV and $\bar{x}$ between $\bar{x}$ and $\bar{x} + dx$ so that $\xi_1, \xi_2, \ldots \xi_{n-1}$ are all positive is

$$\frac{\sqrt{n}}{(\sqrt{2\pi}\,\sigma)^n} \frac{(n-1)}{2^{n-1}} \frac{(\Gamma\frac{1}{2})^{n-1}}{\Gamma\frac{n-1}{2}} \, \text{Exp.} - \frac{nV}{2\sigma^2} \, V^{\frac{n-1}{2}-1} \, \text{Fxp.} - \frac{n}{2\sigma^2} (\bar{x} - m)^2 \cdot dV dx \quad (6)$$

Since $\xi_1, \xi_2, \ldots, \xi_{n-1}$ can take negative values as well we should integrate for negative values also in which case (6) is to be multiplied by 2 for each integration Therefore to get the final distribution of $\bar{x}$ and V (6) is to be multiplied by 2^{n-1}.

It follows from (6) that the distributions of V and $\bar{x}$ are given by

$$\text{A. } \text{Exp.} - \frac{nV}{2\sigma^2} \cdot V^{\frac{n-1}{2}} \, dV \qquad (7)$$

and $\qquad$ B. $\mathrm{Exp.} - \dfrac{n\,(\bar{x}-m)^2}{2\sigma^2} \cdot dx$ $\hspace{2cm}$ (8)

respectively, where A and B are constants which can be easily evaluated.

3. BIVARIATE POPULATION

The frequency distribution in the case of a bivariate population is given by

$$\frac{1}{2\pi\sigma_1\sigma_2\,\sqrt{1-\rho^2}}\,\mathrm{Exp.} - \frac{1}{2\,(1-\rho^2)}\left\{\frac{(x-m_1)^2}{\sigma_1^2} - \frac{2\rho\,(x-m_1)\,(y-m_2)}{\sigma_1\sigma_2}\right.$$

$$\left. + \frac{(y-m_2)^2}{\sigma_2^2}\right\}\cdot dx\,dy = \frac{1}{\sigma_1\,\sqrt{2\pi}\,(1-\rho^2)}\cdot\mathrm{Exp.} - \frac{z^2}{2\sigma_1^2\,(1-\rho^2)}\cdot dz$$

$$\times\frac{1}{\sqrt{2\pi}\,\sigma_2}\,\mathrm{Exp.} - \frac{(y-m_2)^2}{2\sigma_2^2}\cdot dy \hspace{2cm} (9)$$

where $\qquad z = (x - m_1) - \dfrac{\rho\sigma_1}{\sigma_2}\,(y - m_2).$

From (9), as is well known, it follows that the distribution is the product of two independent distributions.

Taking now, a bivariate sample of n observations, let $x_1, x_2, \ldots x_n$ represent the sample of the x-variate, and $y_1, y_2, \ldots y_n$ be the corresponding values of the y-variate. The chance that $x_1, y_1; x_2, y_2; \ldots x_n, y_n;$ should fall within the infinitesimal ranges $dx_1, dy_1; dx_2, dy_2; \ldots dx_n, dy_n$ is

$$\frac{1}{(2\pi)^{\frac{n}{2}}\,(\sigma_1\,\sqrt{1-\rho^2})^n}\,\mathrm{Exp.} - \frac{\sum\limits_1^n z_r^2}{2\sigma_1^2(1-\rho^2)}\,dz_1\,dz_2\ldots\,dz_n\,\times$$

$$\frac{1}{(2\pi)^{\frac{n}{2}}\,\sigma_2{}^n}\,\mathrm{Exp.} - \frac{\sum\limits_1^n (y-m_2)^2}{2\sigma_2^2}\,dy_1\,dy_2\ldots\,dy_n \hspace{1.5cm} (10)$$

$$z_r = (x_r - m_1) - \frac{\rho\sigma_1}{\sigma_2}\,(y_r - m_2)$$

Using (6), the second half of (10) reduces to

$$\text{C.}\quad \mathrm{Exp.} - \left\{\frac{nv_2 + n\,(\bar{y}-m_2)^2}{2\sigma_2^2}\right\}\,V_2^{\frac{n-3}{2}}\,dV_2\,d\bar{y} \hspace{1.5cm} (11)$$

C is a constant

Turning to the first part of (10),

$$\sum\limits_1^n z_r^2 = \sum\limits_1^n w_r^2 + n\bar{z}^2,\; w_r = (x_r - \bar{x}) - \frac{\rho\sigma_1}{\sigma_2}\,(y_r - \bar{y})\;\text{ and }\;\bar{z} = (\bar{x} - m_1) - \frac{\rho\sigma_1}{\sigma_2}\,(\bar{y} - m_2).\quad\text{Again }\sum\limits_1^n w_r^2 = \sum\limits_1^n t_r^2 + n\,(b-\beta)^2\,s_2^2,\, b = \frac{rs_1}{s_2},\, \beta = \frac{\rho\sigma_1}{\sigma_2},\, t_r =$$

$(x_r - \bar{x}) - b(y_r - \bar{y})$, $s_1{}^2$ and $s_2{}^2$ are the variances of the sample (not on the basis of degrees of freedom but on the size).

The above substitutions reduce the first half of (10) to

$$K. \text{ Exp.} - \left\{ \frac{\overset{n}{\underset{1}{\Sigma}} t_r{}^2 + n(b - \beta)^2 s_2{}^2 + n\bar{z}^2}{2\sigma_1{}^2(1 - \rho^2)} \right\} \cdot dz_1 \, dz_2 \ldots . dz_n \quad (12)$$

$$\overset{n}{\underset{1}{\Sigma}} t_r{}^2 = nS_1{}^2 (1 - r^2) = V_{1.2}$$

The method used in the case of the normal population will enable us to show that (12) reduces to the form

$$K_1. \text{ Exp.} - n \left\{ \frac{\overset{n}{\underset{1}{\Sigma}} t^2{}_r + n(b - \beta)^2 s_2{}^2 + n\bar{z}^2}{2\sigma_1{}^2(1 - \rho^2)} - \right\} \cdot V_{1.2}{}^{\frac{n-4}{2}} \, dV_{1.2} \, db \, d\bar{z}. \quad (13)$$

The distribution of $V_{1.2}$, b and $\bar{z}$ are independent of one another.

The product of (11) and (13) gives the joint distribution of $V_{1.2}$, b, $s_2{}^2$, $\bar{z}$ and $\bar{y}$. From this, the joint distribution of $s_1{}^2$, $s_2{}^2$ and r can be easily obtained by omiting the distribution portions for $\bar{z}$ and $\bar{y}$ and finding the Jacobian of

$$\left. \begin{array}{l} f_1 = s_1{}^2 (1 - r^2) - V_{1.2} \\ f_2 = rs_1 - bs_2 \\ f_3 = s_2{}^2 - V_2 \end{array} \right\} \quad J = 2s_1{}^2$$

Substituting this, the distribution of $s_1{}^2$, $s_2{}^2$ and r reduces to

$$L. \text{ Exp.} - \frac{n}{1 - \rho^2} \left\{ \frac{s_1{}^2}{\sigma_1{}^2} - \frac{2\rho rs_1 s_2}{\sigma_1 \sigma_2} + \frac{s_2{}^2}{\sigma_2{}^2} \right\} \cdot s_1{}^{n-2} s_2{}^{n-2} (1 - r^2)^{\frac{n-4}{2}} ds_1 \, ds_2{}^2 \, dr \quad (14)$$

By taking the distributions of $V_{1.2}$, $\bar{z}$ and $\bar{y}$ it is possible to obtain the distribution of generalized Student's Z.

$$\frac{\bar{z}^2}{\sigma_1{}^2(1 - \rho^2)} + \frac{(\bar{y} - m_2)^2}{\sigma_2{}^2} = \frac{1}{1 - \rho^2} \left\{ \frac{(\bar{x} - m_1)^2}{\sigma_1{}^2} - \frac{2\rho(\bar{x} - m_1)(\bar{y} - m_2)}{\sigma_1 \sigma_2} + \frac{(\bar{y} - m_2)^2}{\sigma_2{}^2} \right\}$$

The joint distribution of $V_{1.2}$, $\bar{z}$ and $\bar{y}$ is

$$M. \text{ Exp.} - \left\{ \frac{(nV_{1.2} + n\bar{z}^2)}{2\sigma_1{}^2(1 - \rho^2)} + \frac{n(\bar{y} - m_2)^2}{2\sigma_2{}^2} \right\} \cdot V_{1.2}{}^{\frac{n-4}{2}} \, dV_{1.2} \, d\bar{z} \, d\bar{y} \quad (14)$$

Assuming $\dfrac{\bar{z}^2}{\sigma_1{}^2(1 - \rho^2)} + \dfrac{(\bar{y} - m_2)^2}{\sigma_2{}^2} = \dfrac{T^2}{\sigma_1{}^2(1 - \rho^2)}$, and using Dirichlet's integral,

(14) reduces to $M_1. \text{ Exp.} - \dfrac{n(V_{1.2} + T^2)}{2\sigma_1{}^2(1 - \rho^2)} \cdot V_{1.2}{}^{\frac{n-4}{2}} \, T \, dV_{1.2} \, dT$ \quad (15)

Putting $Z^2 = \dfrac{T^2}{V_{1\,2}}$, (15) becomes

$$M_1. \quad \text{Exp.} - \frac{nV_{1\,2}}{2\sigma_1^2(1-\rho^2)}(1+Z^2)\cdot V_{1\,2}^{\frac{n-2}{2}} Z dV_{1\,2}\, dZ \quad (16)$$

Integrating from 0 to ∞ for $V_{1\,2}$, (16) becomes

$$M_2. \quad \frac{Z\, dZ}{(1+Z^2)^{\frac{n}{2}}} \quad \text{which ultimately is the same as that obtained by}$$

Hotelling.

It can be seen that

$$Z^2 = \frac{\sigma_1^2}{s_1^2(1-r^2)}\left\{ \frac{(\bar{x}-m_1)^2}{\sigma_1^2} - \frac{2\rho\,(\bar{x}-m_1)\,(\bar{y}-m_2)}{\sigma_1\sigma_2} + \frac{(\bar{v}-m_2)^2}{\sigma_2^2}\right\}$$

The real values of σ_1^2, σ_2^2 and ρ are not known; hence in the above test σ_1, σ_2 and ρ are to be estimated from the sample.

From the above discussion it appears that the simplest way of testing the difference between two bivariate samples is to test the significance of the difference between the following by the t test.

1. The difference between the regression coefficients.

2. The difference between the values of $(\bar{x}-m_1) - \dfrac{\rho\sigma_1}{\sigma_2}(\bar{y}-m_2)$ on the basis of the combined variance $s_1^2(1-r^2)$; for $\rho\dfrac{\sigma_1}{\sigma_2}$ the common value for the two samples together can be used.

3. The difference between $(\bar{y}-m_2)$ by using the variance s_2^2.

The assumptions made above will certainly affect the validity of the tests to a certain extent. But as the assumptions are in regard to the ratio $\dfrac{\sigma_1}{\sigma_2}$, $\dfrac{\sigma_1^2}{\sigma_2^2}$ and ρ, they are not likely to affect the tests to any appreciable extent.

4. Multivariate Normal Population

Following Yule and Kendall, the distribution in the case of the multivariate population of n-variates, $x_1, x_2, \ldots x_n$ is

$$\frac{1}{(2\pi)^{\frac{n}{2}}\sqrt{\omega}}\, \text{Exp.} -\frac{\phi^2}{2},\, dx_1\, dx_2 \ldots dx_n,$$

$$\phi^2 = \frac{1}{\omega}\left\{\omega_{11}\,x_1^2 + \omega_{22}\,x_2^2 + \ldots 2\omega_{12}\,x_1\,x_2 + \ldots 2\omega_{n,n-1}\,x_n\,x_{n-1}\right\}$$

$$\omega = \sigma_1{}^2 \sigma_2{}^2 \ldots \sigma_n{}^2 \begin{vmatrix} 1 & \rho_{12} & \cdots & \rho_{1n} \\ \rho_{21} & 1 & \cdots & \rho_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \rho_{n1} & \rho_{n2} & \cdots & 1 \end{vmatrix}$$

$\phi^2 = \dfrac{x_1{}^2}{\sigma_1{}^2} + \dfrac{x_{2\,1}{}^2}{\sigma_{2\,1}{}^2} + \ldots \dfrac{x^n{}_{n\,12\ n-1}}{\sigma^2{}_{n\,12\ n-1}}$, $x_1, x_2, \ldots x_n$ are the deviations from the respective means and $x_{2\,1} = x_2 - \beta_{21} x_1$; $x_{3.12} = x_3 - \beta_{32\,1} x_2 - \beta_{31.2} x_1$; and so on. $\beta_{21}, \beta_{32\,1}$, etc., are the partial regression coefficients.

By proceeding exactly on the same lines as in the case of two variables, the joint distribution can be easily established, for $x_1, x_{2\,1}, \ldots x_{n\,1\,2\,3} \ldots n$ are all independently distributed.

We will now show how the distribution of the generalized Z can be obtained.

$$\dfrac{\bar{x}_1{}^2}{\sigma_1{}^2} + \dfrac{\bar{x}_{2\,1}{}^2}{\sigma_{2\,1}{}^2} + \ldots \dfrac{\bar{x}^2{}_{n.12\ n-1}}{\sigma^2{}_{n\,12\ n\,1}} = \dfrac{1}{\omega}\left\{\omega_{11}\,\bar{x}_1{}^2 + \omega_{22}\,\bar{x}_2{}^2 + \ldots 2\omega_{nn-1}\,\bar{x}_n\bar{x}_{n-1}\right\} = Y \quad (16)$$

$\sigma^1{}_{n\,12\ n-1} = \dfrac{\omega}{\omega_{nn}}\sigma_n{}^2$. The distribution of $V_{n.12\ n-1} = s^2{}_{n\,12,n-1}$ is

M. Exp. $-\dfrac{N\,V_{n\,12\ n-1}}{2\sigma^2{}_{n\,12.\ n-1}} \cdot V_{n\,12\ n-1}^{\frac{N-n-3}{2}}\, dV_{n\,12\ n-1}$ \hfill (17)

By using Dirichlet's integral it can be shown that the distribution of Y is

P. Exp. $-\dfrac{NY}{2} \cdot Y^{\frac{n}{2}-1}\, dY$ \hfill (18)

Taking the joint distributions of (17) and (18) we get

R. Exp. $-\dfrac{N}{2}\left\{\dfrac{V_{n\,12,n-1}}{\sigma^2{}_{n\,12\ n-1}} + Y\right\} \cdot V_{n\,12\ n-1}^{\frac{N-n-3}{2}} Y^{\frac{n}{2}-1}\, dV_{n\,12\ n-1}\,dY$ \hfill (19)

Putting $\dfrac{Y\sigma^2{}_{n.12\ n-1}}{V_{n\,12\ n-1}} = Z^2$, (19) becomes

R_1. Exp. $-\dfrac{N\,V_{n\,12\ n-1}}{2}(1+Z^2) \cdot V_{n\,12\ n-1}^{\frac{N-3}{2}} Z^{n-1}\, dV_{n\,12\ n-1}\,dZ.$ \hfill (20)

Integrating for $V_{n\,12,n-1}$ from 0 to ∞, (20) reduces to

Q $\dfrac{Z^{n-1}}{(1+Z^2)^{\frac{N}{2}}}\, dZ$ \hfill (21)

N represents the size of the sample,

It can be seen that $Z^2 = \frac{\sigma^2_{n.12.\,n-1}}{\omega \cdot s^2_{n.12.\,n-1}} \left\{ \omega_{11} \bar{x}_1{}^2 + \omega_{22} \bar{x}_2{}^2 + \ldots 2\omega_{nn-1} \bar{x}_n \bar{x}_{n-1} \right\}$

$$= \frac{\omega'_{nn}}{\omega_{nn}} \frac{\sigma_n{}^2}{s_n{}^2} \frac{1}{\omega'} \left\{ \omega_{11} x_1{}^2 + \omega_{22} \bar{x}_2{}^2 + \ldots . 2\omega_{nn-1} \bar{x}_n \bar{x}_{n-1} \right\} \qquad (22)$$

If in (22) we substitute the sample values for σ_1, σ_2, etc.,

$$Z^2 = \frac{1}{\omega'} \left\{ \omega_{11}' \bar{x}_1{}^2 + \omega_{22}' \bar{x}_2{}^2 + \ldots . \quad 2\omega'_{nn-1} \bar{x}_n \bar{x}_{n-1} \right\}, \quad \omega', \quad \omega_{11}', \text{ etc. are with}$$

reference to the sample.

As in the case of the bivariate samples, the simplest way of testing the difference between two samples is to test the significance of the following differences by the t test.

(1) The difference between the various regression coefficients.

(2) The difference between the values of x_1, $x_{2\,1}$, $x_{3\,12}$, $\ldots . x_{n\,12} \ldots_{n-1}$; by using the common value of the regression coefficient. The remarks in regard to assumptions made in connection with the bivariate population is true in this case also.

If there are more than two samples, the test can be done by doing the analysis of variance for b's, x_1's, $x_{2\,1}$'s $\ldots . x_{n\,12} \ldots_{n-1}$'s.

5. Distribution of Means of Samples from Type III Population

The expression corresponding to (4) is

$$\frac{1}{(\Gamma p)^n} \text{Exp.} - \overset{n}{\underset{}{\Sigma}} \, x_r \, (x_1 x_2 \ldots x_n)^{p-1} \, dx_1 dx_2 \, \ldots dx_n \qquad (23)$$

Put $\dfrac{x_1 + x_2 \ldots . x_n}{n} = \bar{x}$ and let x_1, $x_2 \ldots . x_n$ take all positive values satisfying the above condition. From (1) it can be easily seen that the chance of $\bar{x}$ lying between $\bar{x}$ and $x + d\bar{x}$ is.

$$\frac{(\Gamma p)^n n^{np}}{(\Gamma p)^n \, \overline{\Gamma np}} \quad \text{Exp.} - n\bar{x} \cdot \bar{x}^{np-1} \, d\bar{x}$$

$$= \frac{n}{\overline{\Gamma np}} \cdot \text{Exp.} - n\bar{x} \cdot (n\bar{x}^{n(p-1)}) \, d\bar{x} \qquad (24)$$

6. Distribution of Means of Samples from Rectangular Populations

(a) *Samples of size two.*—The chance of two observations lying between x_1, $x_1 + dx_1$; and x_2, $x_2 + dx_2$ is

$$dx_1 \, dx_2 \qquad (25)$$

If $\frac{x_1 + x_2}{2} = \bar{x}$, the probability of $\bar{x}$ lying between $\bar{x}$ and $\bar{x} + d\bar{x}$ is

$$4\bar{x}\,d\bar{x} \qquad (26)$$

Since x_1 and x_2 can take values ranging between 0 and 1 only, it is evident that (26) will hold good only so long as $\bar{x} < \frac{1}{2}$. When $\bar{x}$ is greater than half, one of the observed values, say x_1, can be greater than one which is not included in the original distribution, *i.e.*, the range of the original distribution is only from 0 to 1 and this condition is satisfied so long as $\bar{x} < \frac{1}{2}$ and therefore $4\bar{x}\,d\bar{x}$ represents the distribution of the mean only up to $x < \frac{1}{2}$.

Now consider the values of x_1 and x_2 when $\bar{x} > \frac{1}{2}$, x_1 can lie anywhere between 0 and 1 and x_2 between 1 and 2. Evidently the value of x_2 does not come within our population values and therefore that portion of x contributed by the above values of x_1 and x_2 is to be subtracted from $4\bar{x}\,d\bar{x}$. Similarly taking the alternative case of x_2 lying between 0 and 1 and x_1 between 1 and 2 we find that this portion also is to be subtracted from $4\bar{x}\,d\bar{x}$.

It follows from the above discussion that the distribution of the mean in the region x, $\frac{1}{2}$ is given by

$$4\bar{x}\,d\bar{x} - {}_2c_1 \left[\frac{d}{d\bar{x}} \int_1^{2\bar{x}} \int_0^{2\bar{x}-x_1} dx_1\,dx_2 \right] d\bar{x}$$

$$= 4\bar{x}\,d\bar{x} - 8\,(\bar{x} - \tfrac{1}{2})\,d\bar{x}$$

$$= 4\,(1 - x)\,d\bar{x} \qquad (27)$$

(b) *Samples of size n.*—By proceeding on the same lines as in the case of two samples it can be shown that the distribution of the mean of samples of size n consists of different arcs over different sections 0 to $\frac{1}{n}$; $\frac{1}{n}$ to $\frac{2}{n}$ ..... $\frac{n-1}{n}$ to 1 and the equation over the region $\frac{r}{n}$ to $\frac{r+1}{n}$ is

$$\frac{n^n}{\overline{|n}} \left\{ \sum_0^r (-1)^r {}_nc_r \left(\bar{x} - \frac{r}{n} \right)^{n-1} \right\} d\bar{x}. \qquad (28)$$

It may be mentioned that the above expression is identical with those obtained by Hall and Irwin by the use of geometric and characteristic function methods.

The same method enables us to obtain the distribution of the means of samples in the case of Types II, K. $\{x\,(1 - x))^{p-1}\,dx$ and Type I curves, $k_2\,x^{\lambda-1}\,(1-x)^{q-1}\,dx$.

SUMMARY

It has been shown how the well-known Dirichlet's multiple integral can be utilised to derive the distribution of (1) the means and the standard

deviations of samples from normal and multinormal curves; (2) the means
of samples from Types I and III curves.

REFERENCES

Fisher, R. A.	..	*Biometrika*, 1915, **10**, 507.
————	..	*Metron*, 1926, **5**, 90.
Hall, P.		*Biometrika*, 1927, **19**, 240.
Hotelling		*Ann Math. Stat.*, 1932, **2**, 360.
Irwin, J O	.	*Biometrika*, 1927, **19**, 225.
————		*Metron*, 1930. **8**, 51.
Kosambi, D. D		*Curr Sci*, 1941, **10**, 191.
Kullback, S		*Ann. Math Stat.*, 1934. **5**, 263
————		*Ibid*, 1935. **6**, 202
Wishart, J, and Bartlett, M S.		*Proc Camb Phil Soc*, 1932, **28**, 455.
————		*Ibid.*, 1933, **29**, 260
Udny Yule, G, and Kendall, M. G.		*An Introduction to the Theory of Statistics*, 1940, Griffin & Co, Ltd., London.

STUDIES ON THE DEPENDENCE OF OPTICAL ROTATORY POWER ON CHEMICAL CONSTITUTION

Part XXV. The Rotatory Dispersion of Salts of Camphor-β-Sulphonic Acids with Ammonia, o-, m- and p-Nitranilines, Pyridine and p-Aminobenzene Sulphonamide

By Bawa Kartar Singh and Onkar Nath Perti

(Chemistry Department, University of Allahabad)

In a previous communication[1] the study of rotatory dispersion of salts of camphor-β-sulphonic acids with aniline, o-, m-, p-toluidines, α- and β-naphthylamine and ar-tetrahydro-α-naphthylamine was described. In the present paper we have extended this work to camphor-β-sulphonates of ammonia, o-, m- and p-nitranilines, pyridine and p-aminobenzene sulphonamide. The influence of chemical constitution, the nature of the solvent, and wavelength of light on rotatory power has also been discussed.

Schreiber and Shriner's[2] and our previous work[1] have shown that the primary amine salts of camphor-β-sulphonic acids undergo mutarotation in non-aqueous solvents and that it is the result of a structural change in the salt into ketimine or anil. This change is possible only in the case of camphor-β-sulphonates of primary amines and is not possible in the case of salts with secondary and tertiary amines. This view is further supported by our present studies: the camphor-β-sulphonates of primary amines, namely, o-, m-, and p-nitraniline and p-aminobenzene sulphonamide, undergo mutarotation in non-aqueous solvents, whereas those of pyridine, which is a tertiary amine, do not behave in this way as was to be expected (vide Tables IV to VIII).

THE EFFECT OF CHEMICAL CONSTITUTION ON ROTATORY POWER

All the compounds investigated in this paper exhibit " simple dispersion " and obey Drude's one term equation, $[\alpha] = \dfrac{K}{\lambda^2 - \lambda_0{}^2}$. In this equation, K the rotation constant, may be taken as a measure of the rotatory power of the compound for that wavelength (λ) for which $\lambda^2 - \lambda_0{}^2 = 1$ sq. micron. This value of λ_0 is always found to lie in the infra-red region and is slightly greater than 10,000 Å.U. The constant K which is thus independent of the wavelength, may be termed the absolute rotation of the compound. In

Table I the comparative values for $[\alpha]_{5461}^{20°}$ and K (within brackets) are given for different solvents. In Table A the order of rotatory power for position isomerides in different solvents for $[\alpha]_{5461}^{20°}$ is given, the order of K is also given within square brackets.

TABLE A

Solvent		$[\alpha]_{5461}$
Methyl alcohol	.	o- < p- < Un- < m- [o- < p- < m- < Un-]
Ethyl alcohol	.	o- < p- < m- < Un- [o- < p- < n.- < Un-]
Pyridine	..	p- < o- < m- < Un- [o- < p- < m- < Un-]

On comparing values of K the sequence of position isomerides in all the solvents is o- < p- < m- < Un- but for $[\alpha]_{5461}$ the sequence in methyl alcohol is o- < p- < Un- < m-, in ethyl alcohol, o-<p- < m- < Un-, and in pyridine p- <o- < m- < Un. In the comparison of $[\alpha]$ the choice of wavelength 5461 A.U. is quite arbitrary. By selecting different wavelengths different results follow ; thus the order of position isomerides in pyridine for $[\alpha]_{5893}$ is o- < p- < m- < Un-, which is different from that observed for Hg $_{5461}$. These results are neither in agreement with Frankland's " lever arm " hypothesis[9,9a] nor with the electrostatic modification as suggested by Rule[6] according to both of which the *meta* isomer should be intermediate between *ortho* and *para*.

Substituent groups may be arranged according to their polarities Rule[6] has also shown that the arrangement of groups according to their polarities follows a general order, with minor differences, whether the order is deduced from benzene substitution data, influence of various groups on dissociation constant of substituted acetic or benzoic acids or on the basis of electronic theory, and that the order is :

$$\text{O}\overset{-}{\text{H}}, \text{ Cl}, \text{ Br}, \text{ I}, \text{ Et}, \overset{-}{\text{Me}}, \overset{+}{\text{H}}, \text{ COOH}, \text{ CHO}, \text{ COCH}_3, \text{ CN}, \overset{+}{\text{NO}_2}$$
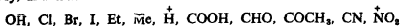
Since the effect of polar groups is traceable on rotatory power,[6] it is found that in general the replacement of a hydrogen atom in an optically active compound by a positive substituent displaces the rotation in the opposite sense to that due to a negative substituent, and further, in general, a positive group should increase the rotation and a negative group should cause a decrease in rotation. In Table B a comparison is made of the effects of —CH₃ and —NO₂ groups, the rotations are given as $[\alpha]_{5461}^{20°}$ and the values of K are also given within brackets.

A4

TABLE B

Camphor-β-sulphonates of	[α]$_{5461}^{Hg}$ in solvent		
	Methyl alcohol	Ethyl alcohol	Pyridine
1 Aniline[1]	32·40 (6·284)	36·40 (6·997)	36·10 (7·57)
2 o-Toluidine[1]	29·60 (5·685)	34·74 (7·93)	36·20
o-Nitraniline	29·97 (3·793)	29·50 (3·666)	31·94 (4·051)
3. m-Toluidine[1]	28·90 (5·661)	34·10 (6·79)	35·50 (7·74)
m-Nitraniline	34·47 (5·882)	35·38 (5·432)	35·97 (5·185)
4 p-Toluidine[1]	30·47 (5·96)	35·50 (6·95)	37·60 (7·81)
p-Nitraniline	30·47 (4·536)	30·42 (4·195)	31·42 (4·782)

On comparing the values of K for pyridine it is found that in all the three cases, *i.e.*, ortho, meta and para substituents, the displacement caused by the electronegative $-CH_3$ group is in the opposite sense to that caused by the electropositive $-NO_2$ group. Comparison of $[α]_{5461}$ in pyridine leads to similar conclusions except in the case of *meta* substituent. The values in other solvents are not in general agreement with the rule probably owing to the solvent effect. True comparisons can, however, be made only in the liquid state in the absence of solvents

The electronegative $-CH_3$ group should cause a decrease in rotation.[6] The results recorded in Table B bear this out. It is found that substitution of $-CH_3$ whether in the o-, m- or p-position causes a decrease in rotation in all the solvents except in the case of *ortho* and *para* substituents in pyridine. On the other hand, the effect of electropositive $-NO_2$ group should be to cause an increase in the rotation.[7] The results given in Table B do not conform to this. Here again, the choice of the wavelength 5461 A.U. is quite arbitrary. If, however, we select the wavelength 5209 A.U. for comparison we find that in pyridine, m-nitranilino camphor-β-sulphonates have higher rotations than aniline salts.

EFFECT OF SOLVENT ON ROTATORY POWER

It is observed (Table I) that for nitraniline salts the order of decreasing rotatory power for Hg$_{5461}$ is pyridine > methyl alcohol > ethyl alcohol > acetone, that for pyridine salts pyridine > methyl alcohol > ethyl alcohol > water, and that for p-aminobenzene sulphonamide salts pyridine <

methyl alcohol > water. With the exception of ethyl alcohol and acetone in the case of nitraniline salts the order of decreasing rotatory power in different solvents runs parallel in the reverse sense with the sequence of the dielectric constants of these solvents.

THE NATURE OF ROTATORY DISPERSION

All the optically active substances described in this paper give " simple[a] dispersion " and can be expressed by one term of Drude's equation, $[\alpha] = \dfrac{K}{\lambda^2 - \lambda_0^2}$. On plotting $1/\alpha$ against λ^2, a straight line was obtained in each case. We have, however, applied the more stringent numerical test by working out these dispersion equations and the results are recorded in Tables III to VIII. It was found that the differences between observed specific rotatory power (o) and that calculated from the equation (c) agreed within

TABLE I

Structural formula	Solvent					
	Water	Acetone	Ethyl alcohol	Methyl alcohol	Pyridine	Chloroform
*R·SO₃H·NH₃	26·50† (3·99)	.	.	.	.	
R SO₃H·H₃N —⬡	20·50 (3 40)	..	36·40 (6·997)	32·40 (6·284)	36·10 (7·57)	45·30 (9·276)
R SO₃H·H₃N —⬡NO₂	..	28·98 (3 502)	29 50 (3 666)	29·97 (3 793)	31·94 (4·051)	
R·SO₃H·H₃N —⬡ (NO₂)	..	30·47 (4·455)	35·38 (5·432)	34·47 (5·882)	35·97 (5·185)	.
R·SO₃H·H₃N —⬡—NO₂	.	28·45 (4·12)	30·42 (4·195)	30·47 (4·536)	31·42 (4·782)	
R·SO₃H·N⬡	26·00 (4·24)	..	38·50 (8·66)	39·96 (8 878)	52 50 (11·24)	.
R·SO₃H·H₃N —⬡—SO₂NH₃	16 97 (2·793)		.	28·00 (4·571)	33 47 (5·611)	

$$\begin{array}{c}\text{CH}_3\text{—}\\ \text{H}_3\text{C—}\text{C—CO}\\[2pt] * \ R = C_{10}H_{15}O \ \text{or} \quad \text{H}_3\text{C—C—CH}_3\\[2pt] \text{H}_3\text{C——CH—CH}_2 \end{array}$$
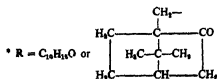
*† Rotations are for Hg₅₄₆₁. The values for rotation constant, k (absolute rotation), are given in brackets.

the limits of experimental error but for the sake of economy of space these differences $(o-c)$ have been omitted in the tables.

THE PHYSICAL IDENTITY OF ENANTIOMERS

The rotatory power of d- and l-forms of these compounds are identical and thus further support Pasteur's principle of Molecular Dissymmetry: out of 472 observations, in as many as 358 cases difference in the numerical value of the specific rotatory power of the opposite isomers corresponds to a difference of less than $0.01°$ in the observed angle of rotation and in 102 cases the corresponding angle lies between $0.01°$ and $0.02°$, which is the limit of experimental error allowed in such measurements ; and only in 10 cases the difference corresponds to between $0.02°$ and $0.03°$, and in two cases the differences are larger ; all these are, however, of the nature of casual experimental errors.

NATURE OF RACEMIC MODIFICATION

The melting points of racemic forms of o- and p-nitraniline and pyridine camphor-β-sulphonates are higher than those of the optically active forms. These racemic forms are, therefore, true dl-compounds in the solid state. In the case of m-nitraniline and p-aminobenzene sulphonamide camphor-β-sulphonates, a small amount of the d-form was added to the racemic modification and the melting point of the mixture was found to be lowered. Thus these racemic camphor-β-sulphonates are also true dl-compounds.[8]

TABLE II

Camphor-β-sulphonates of	Conc in gms/100 cc	$[M]\lambda^{28°}$ in aqueous solution					
		Hg₅₄₅₀	Li₄₆₀₈	Cd₄₆₇₈	Cd₅₀₈₆	Cd₅₀₇₈	A₅₈₁₀₉
1 Ammonium	1 0000		154.4	137.0	122.0	89.64	79.68
2 Pyridine	1.0000	224.9	164.8	150.9	133.8	104.2	96.42
3 p-Aminobenzene sulphonamide	1.0016	260.4	145.2	135.1	119.0	92.16	76.65

Camphor-β-sulphonate of	Conc in gm./100 cc.	$[M]\lambda^{28°}$ in aqueous solution					
		Hg₅₄₆₁	Hg₅₇₈₀	Na₅₈₉₀	Li₆₁₀₄	Cd₆₄₃₈	L'₆₇₆₈
1. Ammonium	1.0000	65.98	54.78	51.05	43.57	38.49	32.37
2. Pyridine	1.0000	80.87	65.31	60.64	55.99	46.66	40.42
3. p-Aminobenzene sulphonamide	1.0016	68.57	58.51	52.46	46.37	40.32	34.26

THE MOLECULAR ROTATORY DISPERSION OF CAMPHOR-β-SULPHONATES
IN AQUEOUS SOLUTION AND COMPARISON OF THE VALUE OF
CAMPHOR-β-SULPHONATE ION IN WATER

Table II gives the values of $[M]_s{}^{35°}$ in water for salts of ammonia, pyridine and p-aminobenzene sulphonamide with camphor-β-sulphonic acid. The mean value[9] for camphor-β-sulphonate ion in water is $[M]_D = 52°$. The value for $[M]_D{}^{35°}$ for ammonium, pyridine and p-aminobenzene sulphonamide camphor-β-sulphonates is 51·05°, 60 64° and 52 46° respectively. This shows that ammonium and p-aminobenzene sulphonamide salts of camphor-β-sulphonic acids are fairly completely electrolytically dissociated in 1% solution but pyridine salts are not so A strict comparison would require, however, a knowledge of degree of ionisation of salts with dilution since the observed molecular rotation is due both to the active ion and the non-ionised molecule.

EXPERIMENTAL

Ammonium-camphor-β-sulphonates[10].—A weighed amount of d-, l- or dl-camphor-β-sulphonic acid was taken in a porcelain dish and excess of liquor ammonia added till the acid was completely dissolved On evaporating to dryness the ammonium salt was obtained. It was then repeatedly recrystallised from a mixture of water and ethyl alcohol The d-, l- and dl-salts which are crystalline are extremely soluble in water but sparingly so in organic solvents. (Found: d-salt, $NH_4 = 7·33\%$; l-salt, $NH_4 = 7·42\%$; dl-salt, $NH_4 = 7·50\%$; $C_{10}H_{15}OSO_3NH_4$ requires $NH_3 = 7$ 23%.)

Nitroanilino-camphor-β-sulphonates[11].Molar amounts of each of the base and the camphor-β-sulphonic acids were dissolved separately in hot ethyl acetate. The two solutions were then mixed and allowed to stand when the salt crystallised out. They were then repeatedly recrystallised from a mixture of ethyl alcohol and ethyl acetate. They were dried at 80° C. in an air oven and then in vacuum. The camphor-β-sulphonates of o- and p-nitraniline crystallise out as yellow coloured needles and of m-nitraniline as white flakes. These salts are freely soluble in ethyl alcohol, methyl alcohol, pyridine and acetone; sparingly so in water and insoluble in ethyl acetate, chloroform and benzene. All yield yellow coloured solutions.

o-Nitroanilino-camphor-β-sulphonates: Found: d-salt, M.P. 117–118° C; $S = 7·80\%$; l-salt, M.P. 116–118° C., $S = 7·93\%$; dl-salt, M.P. 124–125° C., $S = 7·78\%$; $C_{10}H_{15}O_3$. $SO_2H.H_2N.C_6H_4.NO_2.2H_2O$ requires $S = 7·88\%$. m-Nitranilino-camphor-β-sulphonates: (Found: d-salt, M.P. 178–180° C., $S = 8·72\%$; l-salt, M.P. 179–180° C., $S = 8·42\%$; dl-salt, M.P. 171–172° C., $S = 8·79\%$; $C_{10}H_{15}OSO_3H.H_8N.C_6H_4.NO_8$ requires $S = 8·65\%$. p-Nitranilino-

camphor-β-sulphonates: (Found: d-salt, M.P. 155–156° C., S = 7·39%; l-salt, M.P. 154–156° C., S = 7·66%; dl-salt, M.P. 160–161° C., S = 7·50%; $C_{10}H_{15}OSO_3H.H_2N.C_6H_4.NO_2.3H_2O$ requires S = 7·55%.

Pyridine-camphor-β-sulphonates.—Molar amounts of the base and the acid were dissolved in hot ethyl acetate. They were then mixed and allowed to stand in a cool place when the salt crystallised out. They were then repeatedly recrystallised from acetone and dried in vacuum over potash. All the three salts gave white needles.

They are freely soluble in water, ethyl alcohol, methyl alcohol and chloroform; less so in acetone and insoluble in benzene, ether and petroleum ether. (Found: d-salt, M.P. 185–190° C.; eq. wt. = 310·4; S = 10·05%; l-salt, M.P. 185–190° C.; eq. wt. = 315·0, S = 10·40%; dl-salt, M.P. 189–190° C., eq. wt. = 305·9, S = 10·32%; $C_{10}H_{15}$ $OSO_3H.NC_5H_5$ requires eq. wt. = 311·0; S = 10·30%.).

p-Aminobenzene-sulphonamido-camphor-β-sulphonates.—Molar amounts of p-aminobenzene-sulphonamide and camphor-β-sulphonic acids were dissolved separately in hot ethyl acetate. The two solutions were then mixed and allowed to stand. The salts crystallised out. They were repeatedly recrystallised as white needles from a mixture of absolute alcohol and ethyl acetate and dried in vacuum. They are freely soluble in water, methyl alcohol and pyridine; less so in ethyl alcohol and benzene, and insoluble in ethyl acetate, acetone, chloroform, ether and petroleum ether. (Found: d-salt, M.P. 176–182° C., eq. wt. = 408·0, S = 15·96%; l-salt, M.P. 176–181° C., eq. wt. = 400·0, S = 16·14%; dl-salt, M.P. 173–174° C., eq. wt. = 406·0, S = 15·99%; $C_{10}H_{15}OSO_3H.H_2N.C_6H_4.SO_2NH_2$ requires eq. wt. = 404·0; S = 15·84%.)

The d-, l- and dl-sulphonamide salts are being investigated for their pharmacological actions, the results of which will be described in a separate communication.

The rotatory power determinations were made in a 2-dcm. tube. All the determinations of rotatory power were carried out at 35° C. The value of λ_0 calculated from the dispersion formula, is given in the Tables (III to VIII) and is expressed as μ or, 10^{-4} cm.

TABLE III.   *Ammonium-camphor-β-sulphonates in water*

$$[\alpha] = \pm \frac{3\cdot99}{\lambda^2 - \cdot1478} \; ; \; \lambda_0 = 0\cdot3844$$

Temperature 35° C

d-Salt		Line	Calculated [α]	l-Salt	
Concentration in gm 100 c c	Observed [α]			Observed [α]	Concentration in gm 100 c c
1·0000	+93·00°	Hg_5460	94·56	−91·85°	1·0016
	62·00	Li_5400	62·24	62·90	
	55·00	Cd_5078	56·11	55·41	
	49·00	Cd_5100	48 31	55 42	
	36·00	Cd_4800	35·99	35·94	
	32·00	A_5800	32·31	32·44	
	26·50	Hg_5461	26·54	26·96	
	22 00	Hg_5780	21·42	21·46	
	20·50	Na_5898	20·01	19·96	
	17·50	Li_6100	17 76	17·97	
	15·50	Cd_6488	14·96	14·96	
	13·00	L_6708	13·20	13·47	
	No mutarotation			No mutarotation	

TABLE IV.   *o-Nitranilino-camphor-β-sulphonates*

Solvent	Ethyl alcohol	Pyridine	Methyl alcohol	Acetone
Concentration { d- / l- } in gm /100 c c	1·0000 / 1·0016	1·0016 / 1·0000	1·0008 / 1·0000	1·0008 / 1·0000
Calculated { [α] / λ₀ }	$\pm \dfrac{3\cdot666}{\lambda^2-0\cdot1744}$ 0·4176	$\pm \dfrac{4\,051}{\lambda^2-0\cdot1707}$ 0·4132	$\pm \dfrac{3\cdot793}{\lambda^2-0\cdot1713}$ 0·4141	$\pm \dfrac{3\cdot502}{\lambda^2-0\cdot1791}$ 0·4232

Line	Obs [α]^180° d-	l-	Obs [α]^180° d-	l-	Obs [α]^180° d-	l-	Obs [α]^180° d-	l-
Cd_6088	+37·50°	−36·93°	+39·93°	−40·00°	+37·97°	−37·50°	+36·97°	−37·50°
A_5800	29·50	29·94	31·94	31·50	29 97	30·00	28·98	29·00
Hg_5461	23·00	22·46	24·95	25·00	24·98	23·50	23·48	22·00
Hg_5780	21·00	21·46	23·46	23·00	21·43	22·00	20·98	21·00
Na_5898	18·50	18·46	19·46	20·00	18·98	18 50	17·98	18·50
L_6196	15·50	14·48	16·96	16·50	15·48	16·00	14·98	14·50
Cd_6488	13 50	13·98	14·48	15·00	13·98	13·50	12·99	13 50
	Shows mutarotation Rotation for Hg_5461 for d-salt [α]=23·00 after 24 hrs and for l-salt [α] = 22·46 after 49 hrs.		Solution turned dark after 48 hrs		Shows mutarotation Rotation for Hg_5461 after 24 hrs. for d-salt [α] = 22·98 l-salt [α] = 22·00		Shows mutarotation Rotation for Hg_5461 after 23 hrs. for d-salt [α] = 21·48 l-salt [α] = 21 50.	

TABLE V.   m-Nitranilino-camphor-β-sulphonates

Solvent	Ethyl alcohol	Pyridine	Methyl alcohol	Acetone
Concentration $\{$d- $\}$ in gm /100 c c $\{$l-$\}$	1·0032 1·0016	1·0008 1·0016	1·0008 1·0016	1·0008 1·0016
Calculated $\{[a] \}\{\lambda_0\}$	$\pm \dfrac{5·432}{\lambda^2-0·1428}$ 0·3779	$\pm \dfrac{5·185}{\lambda^2-0·1546}$ 0·3932	$\pm \dfrac{5·882}{\lambda^2-0·1294}$ 0·3597	$\pm \dfrac{4·455}{\lambda^2-0·1524}$ 0·3904
Line	Obs $[a]^{86°}$	Obs $[a]^{86°}$	Obs $[a]^{86°}$	Obs $[a]^{86°}$

Line	Ethyl alcohol d-	Ethyl alcohol l-	Pyridine d-	Pyridine l-	Methyl alcohol d-	Methyl alcohol l-	Acetone d-	Acetone l-
Cd_{6438}	+46·85°	−46·92°	+44·96°	−44·42°	+45·46°	−45·92°	+42·46°	−42·43°
A_{5896}	41·86	41·43	35·97	35·94	41·96	41·93	37·47	36·94
H_{6438}	35·38	35·43	28·48	28·95	34·47	34·44	30·47	30·95
$H\beta_{4796}$	28·41	28·95	28·48	28·95	28·47	28·95	24·98	24·96
N_{5896}	26·91	26·45	26·98	26·95	27·47	26·95	22·98	22·46
L_{5461}	23·93	23·46	23·47	23·46	24·47	23·95	19·98	19·96
Cd_{4678}	19·94	19·46	19·98	19·96	20·48	20·96	17·48	16·97
L_{4798}	17·44	17·46	17·48	16·97	18·48	17·46	14·48	14 97

Shows mutarotation. Rotation for H_{6438} for d-salt $[a]=29·41$ after 70 hrs. and for l-salt $[a]=30·45$ after 46 hrs.

Solution turned dark after 48 hrs.

Shows mutarotation. Rotation for H_{6438} for d-salt $[a]=28·48$ after 22 hrs. and for l-salt $[a]=27·45$ after 23 hrs.

Shows mutarotation. Rotation for H_{6438} for d-salt $[a]=25·48$ after 47 hrs. and for l-salt $[a]=25·95$ after 23 hrs.

TABLE VI   p-Nitranilino-camphor-β-sulphonates

Solvent	Ethyl alcohol	Pyridine	Methyl alcohol	Acetone
Concentration $\{$d- $\}$ in gm.·100 c.c. $\{$l-$\}$	1·0024 1·0008	1·0024 1·0008	1·0008 1·0024	1·0016 1·0024
Calculated $\{[a]\}\{\lambda_0\}$	$\pm \dfrac{4·195}{\lambda^2-0·1604}$ 0·4005	$\pm \dfrac{4·782}{\lambda^2-0·1483}$ 0·3854	$\pm \dfrac{4·536}{\lambda^2-0·1500}$ 0·3873	$\pm \dfrac{4·12}{\lambda^2-0·1569}$ 0·3961
Line	Obs $[a]^{86°}$	Obs $[a]^{86°}$	Obs $[a]^{86°}$	Obs $[a]^{86°}$

Line	Ethyl alcohol d-	Ethyl alcohol l-	Pyridine d-	Pyridine l-	Methyl alcohol d-	Methyl alcohol l-	Acetone d-	Acetone l-
Cd_{6438}	+41·89°	−41·47°	+43·39°	−43·46°	+41·97°	−41·89°	+40 93°	−40·39°
A_{5896}	37·41	37·47	38·91	38·47	36·97	37·41	35·93	35·91
H_{6438}	30·42	30·47	31·42	31·97	30·47	30·42	28·45	28·44
$H\beta_{4796}$	25·44	24·98	25·94	26·48	24·98	24·94	23·96	24·44
N_{5896}	22·44	22·48	23·94	23·98	22·98	22·94	21·96	21·94
L_{5461}	19·95	19·98	21·44	21·48	20·48	20·45	19·46	18·95
Cd_{4678}	16·95	15·48	17·95	18·48	17·48	16·95	15·97	15·44
L_{4798}	14·94	14·48	15·94	15·44	15·44	14·94	14·47	14·94

Shows mutarotation. Rotation for H_{6438} for d-salt $[a]=3·42$ after 22 hrs. and for l-salt $[a]=23·98$ after 48 hrs.

Shows mutarotation. Rotation for H_{6438} for d-salt $[a]=28·43$ after 25 hrs. and for l-salt $[a]=27·48$ after 49 hrs.

Shows mutarotation. Rotation for H_{6438} for d-salt $[a]=27·47$ after 22½ hrs. and for l-salt $[a]=27·43$ after 28 hrs.

Shows mutarotation. Rotation for H_{6438} for d-salt $[a]=25·95$ after 25 hrs. and for l-salt $[a]=25·94$ after 24 hrs.

TABLE VII. *Pyridino-camphor-β-sulphonates*

Solvent	Water		Ethyl alcohol		Methyl alcohol		Chloroform	
Concentration $\{d$- l- in gm./100 c c.	1·0000		1·0000		1·0008		1·0000	
	1·0016		1·0016		1·0000		1·0008	
Calculated $\left\{\begin{array}{l}[\alpha]\\\lambda_0\end{array}\right.$	$\pm\dfrac{4\cdot24}{\lambda^2-0\cdot1321}$		$\pm\dfrac{8\cdot66}{\lambda^2-0\cdot0707}$		$\pm\dfrac{8\cdot878}{\lambda^2-0\cdot0760}$		$\pm\dfrac{11\cdot24}{\lambda^2-0\cdot0878}$	
	0·3634		0·2659		0·2757		0·2963	
Line	Obs. $[\alpha]^{28°}$		Obs. $[\alpha]^{28°}$		Obs. $[\alpha]^{28°}$		Obs $[\alpha]^{28°}$	
	d-	l-	d-	l-	d-	l-	d-	l-
Hg5460	+74·00°	−72·88°	+74·00°	−72·88°	+78·43°	−76·00°	+110·00°	−109·94°
L4008	53·00	53·41	62·00	62·40	64·95	64·50	91·00	90·42
Cd6478	48·50	48·92	58·50	58·90	60·95	61·50	87·00	86·42
Cd5800	43·00	43·43	56·00	54·96	56·95	57·50	80·00	79·93
Cd5086	33·50	33·94	46·00	45·93	47·96	48·50	67·00	66·44
A5209	31·00	30·45	43·50	42·93	45·48	45·00	61·00	61·44
H5461	26·00	25·46	38·50	37·94	39·96	40·00	52·50	52·95
H5890	21·00	20·96	33·00	33·44	34·97	35·00	45·50	44·96
N5893	19·50	19·96	31·00	31·45	33·47	33·00	44·00	43·96
L4104	18·00	17·47	28·50	28·45	30·47	30·00	39·50	38·96
Cd6486	15·00	14·47	25·00	25·45	25·97	26·50	33·50	33·97
L6708	13·00	13·48	22·50	22·46	22·48	24·00	20·00	30·47
	No mutarotation		No mutarotation		No mutarotation			

TABLE VIII. *p-Aminobenzene-sulphonamido-camphor-β-sulphonates*

Solvent	Water		Methyl alcohol		Pyridine	
Concentration $\{d$- l- in gm /100 c c.	1·0016		1·0000		1·0008	
	1·0008		1·0016		1·0000	
Calculated $\left\{\begin{array}{l}[\alpha]\\\lambda_0\end{array}\right.$	$\pm\dfrac{2\cdot793}{\lambda^2-\cdot1146}$		$\pm\dfrac{4\cdot571}{\lambda^2-\cdot1322}$		$\pm\dfrac{5\cdot611}{\lambda^2-\cdot1294}$	
	0·3668		0·3636		0·3597	
Line	Obs $[\alpha]^{25°}$		Obs $[\alpha]^{25°}$		Obs $[\alpha]^{25°}$	
	d-	l-	d-	l-	d-	l-
Hg5460	+64·44°	−63·94°	+81·00°	−77·85°	+67·44°	−69·00°
L4008	35·94	36·47	57·00	57·91	35·47	37·00
Cd6470	33·44	32·97	52·00	52·91	61·95	62·50
Cd5800	29·45	28·97	46·00	46·93	55·95	55·00
Cd5086	22·96	22·48	36·00	36·44	42·96	43·50
A5200	18·97	19·48	33·00	32·45	37·97	36·50
H5461	16·97	17·48	28·00	27·95	33·47	33·50
H5890	14·48	13·98	23·00	22·95	27·97	27·50
N5893	12·98	12·99	21·00	20·96	24·98	25·50
L4104	11·48	11·99	18·50	18·97	23·48	22·50
Cd6486	9·98	9·99	16·50	15·97	19·98	19·00
L6708	8·48	8·49	14·00	13·96	16·98	17·50
	No mutarotation		Shows mutarotation. Rotation for Hg5461 for d-Salt $[\alpha]=24\cdot50$ after 24 hrs. and for l-Salt $[\alpha]=23\cdot96$ after 23 hrs.		Shows mutarotation. Rotation for Hg5461 for d-Salt $[\alpha]=28\cdot97$ after 24 hrs. and for l-Salt $[\alpha]=29\cdot00$ after 24 hrs.	

We wish to make a grateful acknowledgment to the Allahabad University for the provision of research facilities and for the grant of an Empress Victoria Readership to one of us (O.N.P.).

REFERENCES

1.	B. K. Singh, O. N. Perti, and B N Singh	*Proc. Lahore Phil. Soc.*, 1944, **6**, 15, reprinted *Allahabad University Studies*, 1944, 37–57.
2.	Schreiber and Shriner	*Jour. Amer Chem Soc*, 1935, **57**, 1306 1445, 1896.
3.	Frankland	*Jour. Chem Soc*, 1896, **69**, 1583
3a	B K Singh and Mazumdar	*Ibid*, 1919, **115**, 567
4.	Rule	*Ibid.*, 1924, **125**, 1122.
5	B. K Singh and B. N. Bhaduri	*Proc. Ind Acad Sci*, (A), 1937, **6**, 340
	Betti	*Gazz. Chim. ital*, 1923, **53**, 424
6.	B. K. Singh and B N. Bhaduri	*Proc Ind Acad Sci*, (A), 1937, **6**, 340
7	——— and T. P. Barat	*Jour. Ind. Chem Soc*, 1940, **17**, 1.
	——— and R. K. Tewari	*Proc Ind Acad. Sci*, (A), 1945, **22**, 20.
8	——— and O. N Perti	*Proc Nat Acad Sci. Ind.*, 1943, **89**, 59
9.	Thomas and Jones	*Ibid. Soc.*, 1906, **89**, 284
10.	Pope and Gibson	*Ibid*, 1910. **97**, 2219.
	Graham	*Ibid.*, 1912, **101**, 746.
11.	Schreiber and Shriner	*Jour. Amer. Chem Soc.*, 1935, **57**, 1306, 1445

SOME STUDIES IN THE SPECTRA OF SINGLE
URANYL HALIDES AND OTHER URANYL SALTS

By D. D. PANT

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received July 12, 1945

(Communicated by Sir C V. Raman, Kt, F.R.S, N L)

1. INTRODUCTION

THE fluorescence of uranyl salts was one of the earliest to be discovered and has been of great interest both in pure and applied research These salts usually fluoresce a copious green and there are many of them emitting fluorescence radiation of varying intensities and spectral characteristics. Luminescence is observed in the crystalline solids, and in various liquid as well as solid solutions. The salts are also found to exhibit several interesting phenomena in fluorescence, *e.g.*, polarisation, long-lived-excitation and so forth. The photochemical reactions brought about by these salts with which the fluorescence and absorption are intimately connected are again of fundamental importance in photo-chemistry.

In view of the wide interest of the subject, therefore, it is no wonder that we find even in the pure spectral studies a long list of prominent workers such as Stokes, E. Becquerel, Morton and Bolton, Hagenbach, J. Becqueral and Onnes and several others. Becqueral and Onnes (1903) greatly advanced the subject by exciting fluorescence at temperatures of liquid air and of liquid hydrogen respectively. This afforded the means of studying the more intimate structure of the spectra and formed, indeed, the starting point for the extensive investigations of Nichols, Howes and their collaborators, the bulk of which invaluable work is collected in the form of a book (1919). Van Heel (1925) excited the fluorescence of uranyl potassium sulphate and autunite by monochromatic radiation and showed the independence of the entire fluorescence spectrum of the frequency of the exciting radiation. Lewischin (1937) has, however, confined his studies only to higher temperatures.

It is curious that the spectra of crystalline single uranyl halides, in spite of their simpler structure, have so far not been studied. The work of Nichols and Howes deals only with the highly fluorescent and more complex salts, *e.g.*, the double chlorides, acetates, sulphates, nitrates and phosphates. Although uranyl chloride did attract the attention of Nichols and Howes, they could not procure the salt in the solid form and have merely

95

studied its spectrum in the aqueous frozen solution at liquid air tempera-
ture. The uranyl halides, therefore, provide us with material for further
experimental investigation which, in view of their simplicity of structure,
is likely to be of use in understanding the complexity of the spectra of
uranyl salts.

With these considerations in view, the spectra of single uranyl halides,
namely, uranyl chloride, two different varieties—one highly and another
weakly flurorescent—of uranyl fluoride and uranyl bromide are studied.
These spectra are found to have some very remarkable features regarding
the intensity distribution in the bands, the peculiar variations in their fre-
quency intervals and in their structure. As these considerations are of great
value for the analysis of the spectra, it is proposed to give here a detailed
account of them. To further elucidate the nature of some of the bands,
the fluorescence spectrum of uranyl chloride has also been studied at various
temperatures. Fluorescence spectra of several other salts, e.g., the nitrate,
the sulphate, the acetate and uranyl potassium sulphate have also been taken
to arrive at a comparison with the spectra of the single halides.

2. MATERIAL FOR STUDY

Excepting the highly fluorescent variety of uranyl fluoride*, all others
are Mackay products (New York). The chloride is yellow in colour, the
bromide brownish yellow, fluoride II greyish green and fluoride I yellow.
Of these, fluoride I has the highest intensity of fluorescence and next in this
order are the chloride, fluoride II and the bromide, the latter hardly emit-
ting any fluorescense at room temperature. The chloride and the bromide
are highly hygroscopic.

Fluoride I was prepared in a manner described by W. S. Andrews
(cf. Mellor, 1932). A solution of 12·5 gm. of uranyl nitrate in 50 c.c. of
water was mixed with 19 gm of ammonium fluoride dissolved in 28 c.c.
of water. The precipitate was repeatedly washed with cold water. The
salt after drying gave bright green fluorescence. A qualitative chemical
test was made to assure that both the Mackay and the present products
were fluorides.

3 EXPERIMENTAL ARRANGEMENT

The arrangement for studying the fluorescence spectra at low tempe-
ratures was quite simple. The salt was placed in a long pyrex glass tube,
the sealed end of which was slightly bent and possessed a plane surface.
Light from a carbon (or iron) arc after having been filtered through a

---

* Called hereafter fluoride I, the weakly fluorescent variety being fluoride II.

Wood's glass to cut off the interfering portion of the visible spectrum and through a water cell to absorb the infra-red light, was focussed on this surface. The latter was so oriented as to allow maximum intensity of fluorescence to be condensed on the slit of the spectrograph. The portion of the tube containing the salt was completely immersed in liquid air contained in a transparent cylindrical Dewar flask. The absorption due to liquid air was unavoidable but was reduced to a minimum by keeping the flat face of the tube close to the near side of the Dewar flask. The absorption bands of liquid air, however, did not fall on the location of the important bands. In another method, use was made of a joined copper and wooden rod to avoid the absorption and the intensity loss due to the scattering by liquid air. A rectangular slot with a hole in the middle was made in the copper portion of the rod. The latter was held vertically by clamping the wooden portion, while the copper rod was immersed in liquid air contained in the Dewar flask. A small glass cell which contained the salt was placed tightly in the slot. The cell was made out of two small rectangular glass plates cut to the size of the slot, which were sealed on the edges by beeswax. The filtered ultra-violet light was focussed on the cell The disadvantage of this method, however, is that the temperature attained by the salt is not exactly the same as that of liquid air.

For absorption experiments, a thin layer of the salt was placed in the cell. The latter was completely pasted with black paper on all sides except for a small hole in the middle. The cell was mounted on the slot and the filament of a tungsten lamp was focussed on the hole. The transmitted light was focussed on the slit of a Fuess spectrograph. Varying thickness of the salt had to be taken to get the spectra in the various regions.

The fluorescence spectra to be discussed below are all obtained by the first method except the spectrum of fluoride II which has been taken by the second method. Exposures varying from 9 hours for fluoride II to 15 minutes for uranyl potassium sulphate were necessary to get the spectra.

4. FLUORESCENCE SPECTRA AT LIQUID–AIR TEMPERATURE

Tables I, II and III contain the measurements of wave-lengths of the fluorescence bands of uranyl chloride, fluoride I and of fluoride II respectively. The four most intense bands are designated as B, C, D and E, the notation differing from that of Nichols and Howes who have given different designations to the same series of bands observed in different salts. The D band is not present in the fluoride II spectrum (see Figs. 2 *a* to 2 *g*). For convenience, the fluorescence spectra of uranyl chloride, uranyl fluoride I

<div align="center">D. D. Pant</div>

TABLE I. *Fluorescence Bands of Uranyl Chloride at — 185° C.*

Int	Desig.	Group	ν	Int.	Desig.	Group	ν
0			20589	1	A		18947
2			20565	0	B	3	18834
9	B		20535	0			18803
0		1	20511	10			18777
2			20482	7	C		18709
1	C		20462	2	D		18634
1			20440	6	E		18536
6	D		20339	0	I		18107
8	E		20286	0	A		18069
0			20240	8	B		17905
0			20218	8	C		17835
1	F		20130	2	D	4	17778
2	F'		20093	0	E		17694
1	G		20051	5			17663
1	A	2	19833	0			17608
1	B		19716	1	I		17249
1			19685	3	B		17030
10			19655	0	C	5	16956
0			19628	1	D ?		16630
6	C		19574	2	E		16785
6	D		19489	0	A		16341
6	E		19405	1	B	6	16155
				2	C		16090

TABLE II. *Fluorescence Bands of Fluoride 1 at — 185° C.*

Int	Desig.	Group	ν	Int.	Desig.	Group	ν
6	B		20095	8	E		18286
10	C		20012	1	F'		18198
3	D		19967	1	G	3	18065
4	E	1	19912	2	I		17923
0	F'		19794	1			17780
3	G		19728	0	A		17686
1	H		19661	5	B	4	17736
3	I		19578	3	D		17573
10	B		19274	10	C		17523
12	C		19183	8	E		17457
–	D		19171	0	F'		17399
8	E	2	19112	1	H		17235
1	E'		19028	0	I		17085
3	G		18846	1	A		16881
1	H		18764	2	B		16819
4	I		18718	2	D	5	16786
1	A		18521	8	C		16696
8	B	3	18455	5	E		16641
3	D		18390	0	C		15878*
10	C		18345	0	E	6	15821*

* Visually estimated values.

TABLE III. *Fluorescence Bands of Fluoride II at* $-185°$ C.

Int.	Desig.	Group	ν	Int	Desig	Group	ν
0	A	1	20234	4	C	3	{ 18289
8	B		20082				{ 18263
2	A		19366	0	A	4	17641
10	B		19217	4	B		17492
4	C	2	{ 19150	4	C		{ 17404
0	E		{ 19124				{ 17427
			18970 ?	0	B	5	16640*
1	A	3	18504	0	C		16577*
9	B		18353				

* Visually estimated values

and II are drawn to scale separately, where only the important bands are
shown (Figs 1 *a*, *b* and *c*).

No fresh measurements have been made for the fluorescence bands of
the acetate, the nitrate and the sulphate. The values given by Nichols and
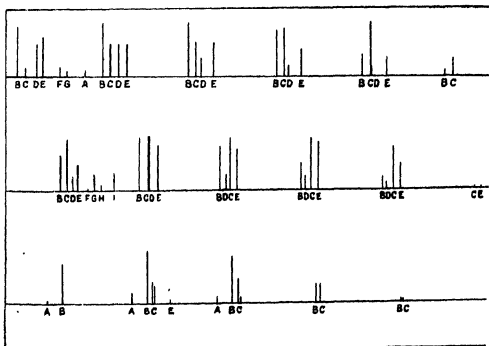
FIG 1. Some important bands in the fluorescence spectra of (*a*) uranyl chloride.
(*b*) uranyl fluoride I and (*c*) uranyl fluoride II

Howes are taken as correct. We do, however, find minor differences in the intensities of the bands given by them and those observed here. The E_0 (*i.e.* the E band of the first group) band in the nitrate (B band of Nichols and Howes) is reported to be strong by these authors, while we find it to be extremely weak. No trace of D bands (C of Nichols and Howes) could be detected. The intensities of the A bands in the spectrum of the sulphate also do not quite agree with ours. Similar deviations have also been found in uranyl potassium sulphate. Comparison of spectra shows that all except the fluoride I spectrum are rather complex. They all fall into groups each consisting of several members. Out of these the four members, namely B C, D and E, seem to be most important on account of their high intensity. The whole spectrum appears to be a repetitive pattern of a group of these bands. There is a general resemblance in all the spectra so far as the B and C bands are concerned. Minor variations in intensity, frequency intervals and the position of the spectra are, however, present.

The spectrum of fluoride I differs from that of fluoride II. The B bands of the first group (the electronic frequency) fall approximately at the same region in both the cases. While A band is missing in fluoride I spectrum, it is present with appreciable intensity in the other case. The D band is absent in the latter while it has moderate intensity in the former. The frequency intervals are also different in the two spectra. The fluoride I spectrum is very much more complicated than that of fluoride II.

It is interesting to find that sometimes two entirely different salts give nearly identical spectra both with respect to the wave-length measurements and the intensity distribution of the bands. Thus, the spectra of fluoride I and anhydrous acetate (Nichols and Howes, *loc. cit.*) are nearly identical. The number of bands present in the spectrum of anhydrous acetate is how-ever, greater. The B, C, D and E bands of uranyl nitrate (E, D, C, B bands of Nichols and Howes) and uranyl acetate (F, E, D, C of Nichols and Howes) are nearly identical as can also be seen from Figs. 2 *d* and *c* where only B and C bands have appeared with high intensity.

These four bands show some very interesting behaviour in the various groups, specially in the spectra of the chloride and fluoride I where peculiar variations in intensity and frequency intervals are observed. Both these aspects will be discussed for these two spectra in the following sections.

5. CHANGES IN FREQUENCY INTERVALS

In the uranyl chloride spectrum, the D band is seen continuously shift-ing towards the B or C bands. The distance B–D which is 196 cm.$^{-1}$ in the

first group has diminished to 72 cm.$^{-1}$ in the 4th group with the result that both the D and C bands have practically coalesced into a broader band. Similar peculiarities are observed in the spectrum of fluoride I and can be seen visually without any recourse to wave-length measurements   In the 1st group the C and the D bands are separated out by 45 cm.$^{-1}$ In the 2nd they come close together and form a single broad band. The separation again occurs in the 3rd group and goes on increasing in the higher groups. The C band, thus, shifts towards the right while the D band shifts towards the left in the successive groups.

6. Intensity Distribution

In general, the intensity of the bands reaches a maximum in the 2nd group after which there is a continuous decrease. However, all the bands do not behave alike in this respect. It is better therefore to examine each band series separately.

The B band is most intense in the lower groups. It attains the maximum intensity in the 2nd, after which there is a regular fall in its intensity.

The most interesting case is presented by the C band. It has such a small intensity in the 1st group that it is hardly visible.   In the 2nd group, the band suddenly becomes very intense The maximum intensity is probably attained in the 3rd or the 4th group which, however, falls down rather slowly in the higher groups. Thus, the C band which is the weakest in the 1st group, remains the most intense band in the last group.

The D band usually starts with maximum intensity which, however, falls down very rapidly in the higher groups. There is nothing very remarkable in the behaviour of the E band. In the spectrum of fluoride I, however, the E band behaves in a manner similar to the C band. In other spectra the D and the E bands are weak in intensity The B and C bands behave as stated above, C band in fluoride I spectrum starts with high intensity.

Out of the less important bands, particular mention may be made of the A bands. In the chloride spectrum, the A band is missing in the 1st group, but it appears with sufficient intensity in the 2nd, thus resembling the C band. The phenomenon is more evident in the spectrum of the sulphate (Fig.1 *f*) where the A band can be seen between two successive groups. It also looks that the presence of the A band makes the increase in the intensity of the C band less prominent.

7. Other Details

An interesting feature, which is prominently observed in the uranyl chloride spectrum, is the accompaniment of diffuseness or a featureless

short continuum. The first group of bands will be seen to be recorded on a more or less clear background except that the D band is only slightly diffuse. The bands of the 2nd, 3rd and the 4th groups, on the contrary, are accompanied by an extended diffuseness on account of which many weak bands have been masked. The 5th and the 6th groups are again free from it. It will be noted that these latter groups do not contain the D band. The diffuseness is thus evidently connected with the latter. In the fluoride I spectrum, specially in the 2nd, the 3rd and the 4th groups, the D band produces a very short but intense diffuse background extending up to the F' band. In uranyl potassium sulphate the diffuseness is again very marked (Fig. 4 a). In other spectra the D band is less prominent and so also is the diffuseness.

It will further be seen that the structure of all the bands is not the same. The C and E bands in the chloride spectrum in the 2nd and the 3rd groups are decidedly broader than the B band. They have moreover exactly the same appearance (Fig. 2 a). The similarity in these bands is much more marked in the fluoride I spectrum.

In some spectra (Fig. 2 f) each strong band is accompanied on both the sides of it by several closely spaced (nearly 30 cm.$^{-1}$) sharp bands. This gives a remarkable appearance to the band. This will be very easily appreciated by examining the B and E bands of uranyl sulphate.

8. Effect of Temperature Variation on the Fluorescence Spectra

For a clear understanding of the nature of the diffuse background produced by the D bands, further investigation is absolutely necessary. The obvious method for progresss in this direction, is no doubt, to study the effect of temperature variation in these bands. We report below some results obtained in this connection with uranyl chloride and uranyl potassium sulphate. All the spectra except one (to be pointed out later) were photographed by the first method. The various temperatures were obtained as per Table IV

Uranyl chloride being highly hygroscopic had absorbed considerable water and had to be recrystallised to get it in the solid form. The solution to which a few drops of concentrated hydrochloric acid were added was evaporated by slowly heating it over a small flame. This highly concentrated solution was kept in a desiccator containing concentrated sulphuric acid. Quite large crystals, although slightly moist, were picked up in the experimental tube.

TABLE IV

Temperature	Method of obtaining it
−185° C.	Liquid-air temperature.
−110° C	Absolute alcohol was contained in the Dewar flask. The thermocouple junction and a glass stirrer were dipped into it. Liquid air was poured slowly till after constant stirring ice of alcohol was formed on the top. The time of appearance of the temperature was noted by the help of the thermocouple and a galvanometer.
−70° C. or and other temperature	By adding proper amount of liquid air to alcohol any required temperature can be obtained. The temperature has to be kept constant by adding liquid air from time to time.
30° C	Room temperature
	The temperatures were read by a calibrated galvanometer and are probably accurate within 5° to 7° C

Figs. 3 *a*, *b* and *c* give the spectra of uranyl chloride at 30° C.–70° C. and − 110° C. respectively while Figs. 3 *d* and *e* are the spectra of the same salt at − 185° C. It will be observed that the D band is absent at the higher temperatures and just begins to appear at liquid air temperature still unresolved and accompanied by a continuum. The time of exposure for the lower spectrum is higher. The continuum is decreased and the D band is also seen faintly present as a resolved band. Spectra given in Figs. 3 *f* and *g* are taken with perfectly dry salt. The upper one is taken by the second method and the lower one by the first. The remarkable increase in the continuum which starts now even in the first group after the D band, is obviously due to the temperature of the salt in the former case being slightly higher than − 185° C. We have, however not measured it. It will be noted that while there is no contrast in the resolution of the B, C or E bands in the spectra of the dry and the moist salt, the D band behaves differently. The liquid air temperature appears to be the transition point for the appearance of the D bands.

At higher temperatures, there is a definite tendency for the B, C and E bands to broaden out. There is also a continuous shifting of the bands towards the red. At room temperature a new band appears on the high frequency side. All other bands except this are double. The following table gives the measurements of the bands observed at room temperature.

The frequency intervals also get decreased at higher temperatures. At boiling water temperature all the bands except the first merge in a continuum. The salt also loses its fluorescence. We have not recorded this spectrum.

TABLE V

Int	Group	Desig	ν	Int	Group	Desig.	ν
1	0		20963	10	3	B	18620
						E	18404
8	1	B	20432				
		E	20131	9	4	B	17770
						E	17536
10	2	B	19518				
			19326	8	5	B	16907
						E	16718

The salt seems to lose its water of crystallisation, for, if such crystals are moistened or if the salt is allowed to cool to reabsorb its water of crystal-lisation, fluorescence is again observed.

The spectrum of uranyl potassium sulphate at $-185°$ C. (Fig. 4 a) shows a similar diffuseness as the chloride spectrum. The D band which causes the diffuseness is most probably the weak one just to the short λ side of the 3rd band which is the B band. At $-110°$ C. (Fig. 4 b), the D band is practically missing, if not completely The extension of the diffuseness is also less marked, although there is a general broadening of the bands. Indeed, it would be of interest to see if the D band appears more resolved and the diffuseness disappears also at temperatures lower than $-185°$ C.

9. THE FLUORESCENCE SPECTRUM OF URANYL BROMIDE

The fluorescence spectrum of uranyl bromide has its own character-istics and has therefore not been discussed along with the other spectra. Even visually the salt is different in several respects from other uranyl salts. Besides its colour and practically non-fluorescent characteristic, the salt is available in the form of a plastic solid rather than as crystalline powder. The peculiar property of uranyl bromide in which it differs widely from other uranyl salts is its tremendous increase in fluorescence when cooled to liquid air temperature. A comparison with the fluorescence properties of uranyl fluoride II will make the case obvious. The bromide fluoresces even more weakly than fluoride II at room temperature, while at liquid-air temperature its intensity of fluorescence is a hundred times more than that of the latter. The observed spectrum is also of an unusual nature. There are not well resolv-ed and sharp bands as observed in other cases. Except for the three bands namely A, B and D at 20390, 20249 and 20105 (in wave numbers) respectively, which form the first group, the spectrum, on the long wave-length side, has the appearance of a continuum. In reality, however, the spectrum consists of 6 groups of bands only more diffuse and broadened

out than those observed at room temperature in the case of other salts. The frequency interval in the successive group has approximately been estimated to be 870 cm.$^{-1}$ In the 2nd group, two bands still stand out inside the continuum (Fig. 2 g).

10. ABSORPTION SPECTRA AT LIQUID–AIR TEMPERATURE

(a) Uranyl Chloride

Fig. 5 a shows the absorption spectrum of uranyl chloride taken with a thin layer (·05 mm.) of the salt. The various parts of the spectrum have been obtained by varying the time of exposure. Figs 5 b and c which give the absorption spectra with 0·21 mm. and 0·6 mm. thick absorbing layers, show how the spectrum is affected on increasing the thickness of the absorbing layer New bands appear on the long wave-length side while the bands on the shorter wave-length side cannot be seen on account of a heavy general absorption. Besides these, some intense bands appear with a prominent structure. They are accompanied on both the sides by a number of sharp and closely spaced (nearly 40 cm.$^{-1}$) bands.

In Table VI the absorption bands obtained from several plates are listed. It is not possible to give the relative visual intensities of the bands, but the stronger bands have been marked in the table.

TABLE VI. *Absorption Bands of Uranyl Chloride*

Desig.	ν	Remarks	Desig.	ν	Remarks
F	20132			21855	
E	20270 ⎫		c	21905	
D	20338 ⎬	Observed with thick layers only	b	21985	
C	20439 ⎭			22054	
	20511			22115	
b (B) ⎰	20534		a	22201	
	20562		e	22201	
	20760		f	22351	Strong
	21096			22507	
	21118			22641	Medium
	21165		b	22733	
c ⎰	21205	Strong band having close companions		22794	
	.1747		f	23097	
b	21287			23226	
	21328			23328	
a	21402		c	23382	
e	21505		j	23838	Strong
f?	21546	Beginning of a new series		23943	
	21716		c	24054	
	21776		f	24567	Strong
			c	24787	
			f	25293	
			e	25509	

The absorption spectrum (Fig 5 *a*) for a thin layer is of much simpler appearance than the complicated spectra observed with thick layers. The absorption begins at 20535 cm.$^{-1}$ and extends towards the shorter wavelengths. On examination, it will be seen that the whole spectrum consists of three series of bands, namely *b*, *c* and *f*, having fairly long progressions. Some noteworthy points about the spectrum are the appearance and the increase in intensity of some series as we proceed towards the ultra-violet. Thus the *f* series starts quite in the middle of the spectrum and possesses the strongest bands till the last. The *c* band is not present in the first group but it has a high intensity in the second and continues to appear till the last. The bands thus resemble the *c* bands of the fluorescence spectrum. The *b* bands have got nearly the same intensity in the lower groups, while in the higher groups they are practically absent   The bands in general get broader towards the ultra-violet.

(b) Uranyl Fluoride II

Table VII contains the absorption bands of uranyl fluoride II. The thickness of the absorbing layer does not have the same effect as in the

TABLE VII.   *Absorption Bands of Uranyl Fluoride II*

Desig	ν	Remarks	Desig	ν	Remarks
b (B)	20082		b	22190	
a (A)	20234			22352	
f	20475		a	22418	
b {	20762	Two close, comparisons		22726	New type of absorption series starts
	20781			22823	
	20809			22885	
a	20951		f	22943	
f	21188		b	23003	
b {	21481	Two close compa-risons		23441	
	21534			23539	
	21682			24154	
f	2193?				

previous case except that on account of the general absorption weaker bands in the ultra-violet do not come out. There are twelve absorption bands in the region between 4980 Å and 4415 Å. Three bands, namely *b*, *a* and *f* form a group. The first group consists of two distinct sharp bands and of a very faint absorption region at about 4878 Å (Fig. 4 *c*). In the second group the first band is accompanied by two closely spaced lines (nearly 20 to 30 cm.$^{-1}$). The second band becomes more diffuse while the third most. The diffuseness increases further in the ultra-violet. After 4399 Å a new type of absorption begins consisting in a number of rather close bands. There are

three such bands occurring at interval of nearly 700 cm.$^{-1}$ These bands are very weak, and hence their wave-lengths have been only visually estimated.

11. OVERLAPPING REGION OF FLUORESCENCE AND ABSORPTION SPECTRA

An interesting fact about the fluorescence and the absorption spectra of the uranyl salts is their apparent symmetry about the B band of the first group. In the spectrum of uranyl chloride for example, the fluorescence spectrum lies towards the red of the B band at 20535 cm.$^{-1}$ while the absorption spectrum extends towards the ultra-violet. Thus only the B band is observed both in fluorescence and absorption. With greater thicknesses of the absorbing layer, the absorption spectrum can be pushed more towards the red and a number of bands which appear in fluorescence can now also appear in absorption. This phenomenon has also been observed by Nichols and Howes who call it a double reversal. In the present case, it will be seen that (with a ·6 mm. thick layer of the salt) the B, D, C and the F bands belonging to the first group of fluorescence spectrum have also been obtained in absorption (Fig 4 *f*).

The fluorescence spectrum of uranyl fluoride, it will be seen, has a weak A band on the higher frequency side of the B band which in the uranyl chloride spectrum is absent. In absorption, both these bands are observed (irrespective of the thickness of the absorbing layer) with the important difference that the weak A band now appears as a strong band while the strong B band appears weak (Fig. 4 *e*). Increasing the thickness of the salt does not have the effect of further pushing the spectrum towards the red, since there are no fluorescence bands in the first group after the B band.

Similar remarks apply to the spectra of uranyl bromide where the A and B bands of the first group of the fluorescence spectrum are again observed in absorption with reversed intensities (Fig. 4 *d*). The third D band appears to be present in absorption also, but the frequencies of the two do not coincide. A slight difference in temperatures which is bound to be present in the two cases, may account for this.

In conclusion, the author expresses his gratitude to Sir C. V Raman, for his keen interest during the course of the investigation. His thanks are also due to Mr. G. R. Rendall for his assistance in preparing the plates.

SUMMARY

The fluorescence spectra at liquid-air temperature of crystalline uranyl chloride, uranyl fluoride I and II, and of uranyl bromide have been studied

for the first time. The spectra of uranyl acetate, nitrate, sulphate and uranyl potassium sulphate have been taken for comparison. Out of the several series present, B, C. D and E are pointed out to be most important. A remarkable shifting of the D band as well as peculiarities in the intensity distribution are noticeable. The similarity between the C and E bands and the extended diffuseness produced by the D bands are also noteworthy.

A slight rise in temperature from −185° C. causes a great increase in the diffuseness produced by the D bands. With moist crystals the D band appears as a short continuum even at − 185° C. but at − 110° C. and − 70° C. only B, C and E are present, the D bands completely disappear Uranyl bromide has been found to increase tremendously in intensity on cooling, its spectrum at −185° consisting of very broad bands giving an appearance of a continuous spectrum.

The absorption spectra of uranyl chloride have been taken with varying thickness of the absorbing layer. With thick layers, some bands which are observed in fluorescence can also be obtained in absorption. In the absorption spectrum of uranyl fluoride II and uranyl bromide the first two A and B bands of the fluorescence spectra appear as A and B band in absorption with a remarkable reversal of intensity.

REFERENCES

1 Nichols and Howes   . *Fluorescence of Uranyl Salts*, Carnegie Institute Publication, No. 298, 1919.
2 Van Heel   *Leiden Communications*, 1925, Suppl. No. 187 A.
3. Tewschin   *Acta Physico Chimica, U.R.S.S*, 1937, **6**, 661
4. Mellor   *Treatise on Inorganic and Theoretical Chemistry*, 1932, **12**, 76

(a)

(b)

(c)

(d)

(e)

(f)

(g)

Fig. 2

Fig. 3

(a)

(b)

(c)

(d)

(e)

(f)

Fig. 4

(a)

(b)

(c)
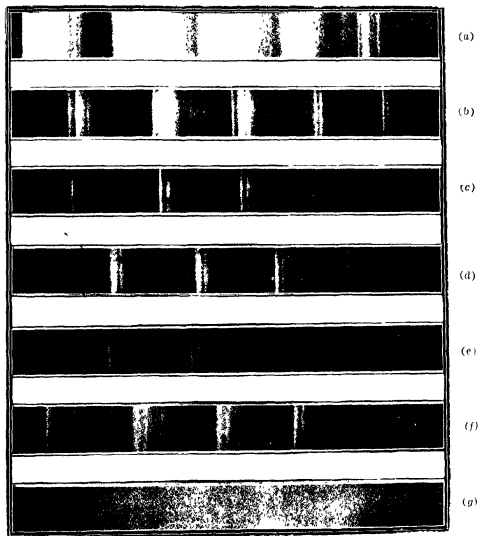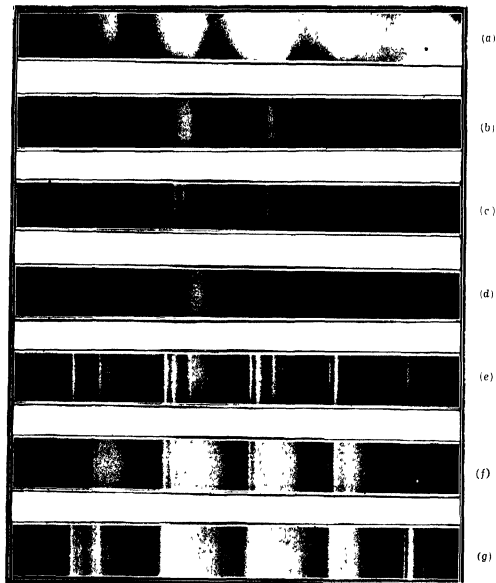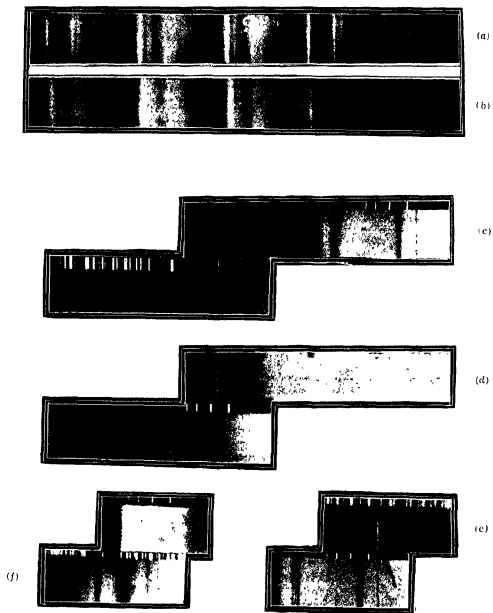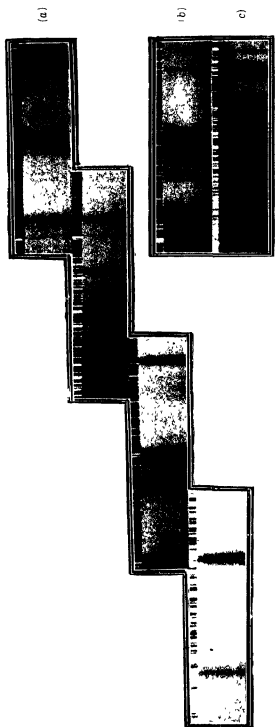
Fig. 5

DESCRIPTION OF PLATES

Plate III

Fig 2 Fluorescence spectra at −185° C. Equally enlarged and arranged to scale to show the variation of electronic frequency from salt to salt—(a) chloride : mark the behaviour of the C and the D bands ; (b) fluoride I : C is shifting to the right while D to the left in the successive groups ; (c) fluoride II : weak A band to the left of the strong B and the absence of the D band will be noted ; (d) acetate : the two intense B and C bands will be seen ; (e) nitrate · compare (d) and (e) , (f) sulphate · mark the several close companions of B and E bands ; the A band will be seen between any two successive groups ; (g) bromide : compare with the other spectra ; A, B and D bands are seen in the extreme left.

Plate IV

Fig. 3. Fluorescence spectra of uranyl chloride (moist)—(a) at 30° C.: mark the weak band on the extreme left ; (b) and (c) at −70° C. and −110° C respectively · B, C and E are present, D is missing ; (d) at −185° C, D appears in the form of a short continuum ; (e) at −185° C : with a longer exposure D appears weakly as a line also ; (f) spectrum of not moist salt taken by the 2nd method at −185° C : note the high intensity of the diffuseness ; (g) spectrum of not moist salt taken by the first method · D band is resolved.

Plate V

Fig. 4. Fluorescence spectra of uranyl potassium sulphate—(a) at −185° C : mark carefully the B, C, D and E bands ; (b) at −110° C ; (c) absorption spectrum of fluoride II at −185° C , (d) overlapping region in the fluorescence and absorption spectra of bromide : A, B, D bands are present in both ; A and B have reversed intensities ; (e) fluoride II : A and B again with reversed intensities , (f) chloride : with thick layers ; C, D and E have been also obtained in absorption.

Plate VI

Fig. 5. Absorption spectra of uranyl chloride at −185° C.—(a) with ·05 mm thick layer · note the b, d and f series ; (b) with ·21 mm, thick layer · (c) with ·6 mm. thick layer,

ANALYSIS OF THE FLUORESCENCE BANDS OF THE URANYL SALTS

By D. D. PANT

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received July 13, 1945

(Communicated by Sir C V. Raman, Kt, F R S , N L)

1. INTRODUCTION

IT has been known for a long time that the fluorescence spectra of uranyl salts at low temperatures consist of several discrete and sharp bands which usually fall into six regularly spaced groups. The bands contained in a group are the members of the several series which have been earlier designated as A, B, C, D, E, etc. The frequency interval between the two successive members of the same series is nearly 860 cm.^{-1} which in the complementary absorption spectra diminishes to nearly 700 cm.^{-1} These intervals, however, vary slightly from one spectrum to another, and sometimes regular as well as irregular variations in them are also noticed from series to series in the same spectrum.

The regularity in the spectra and the fact that only those compounds of uranium which possess the uranyl group are fluorescent, led Nichols and Howes (1919) to suggest that the constant frequency intervals were due to the uranium oxide. Several arguments can now be advanced in favour of this suggestion and particularly the appearance of the 860 cm.^{-1} frequency in the Raman and infra-red spectra of uranyl salts (Conn and Wu, 1938; Satyanarayana, 1942) leaves no doubt as to its correctness. The earlier contention of Dieke and Van Heel (1925) that the constancy of the frequency intervals is due to a simultaneous change of the electric moment and the oscillation of the nuclei of the UO_2 group is also, therefore, correct. The difficulty of explaining the large number of bands and the smaller frequency intervals, however, still remains on this simple idea. In a subsequent paper Van Heel (1925) assuming the existence of one more frequency which he attributed to the vibration of UO_2 in the crystalline space lattice attempted an interpretation of the bands, but no further work seems to have been done in this direction since then. As is indicated by a remark by Pringsheim (1933) that Van Heel's analysis is analogous to that for the benzene spectrum, presumably his interpretation has finally been taken as satisfactory. This, however, is not true for several reasons to be given in the following section where Van Heel's analysis is discussed in detail.

2. REMARKS ON VAN HEEL'S ANALYSIS

Van Heel has interpreted the spectra at liquid-air temperature of only uranyl potassium sulphate and autunite. In the former case, two frequencies N and P representing respectively the oscillation frequency of the nuclei and the vibrational frequency of UO_2 in the crystalline space lattice have been taken. N = 833 cm. [1] and 678 cm. [-1] respectively in the ground and the excited states and its quantum number can change by any integer, e.g., 0, 1, 2, 3, etc. P = 77 in the ground state and not more than one quantum of this frequency takes part In the excited state without any change in its quantum number, the value of this frequency changes to 88, 113, 127, 137, 144, 149 and 149 cm.[-1] in the successive group This would, of course, lead to the assumption of a peculiar type of anharmonicity factor where the frequency of vibration changes without any change in its quantum number, but may still be understood as being due to an extremely strong coupling between the N and P vibrations. This apart, the transitions from (2, 0), i.e., N = 2 and P = 0, in the excited state to (6, 0) or (7, 0) in the ground state have little significance when the spectrum extends only up to the 6th group (i.e., N = 5). Some several relatively strong bands also do not find a place in the analysis. But as we have very little knowledge of the coupling together of the electronic and vibrational energies in the condensed state of matter and also of the various complicated factors that may influence the energy states, the discrepancies outlined above should not be stressed too far. The most outstanding objection to the term scheme, however, is that it is in contradiction with the experimental results. Van Heel's own observations show that the entire fluorescence spectrum appears when the frequency of the exciting radiation equals the electronic frequency It is also known that whatever may be the frequency of the exciting radiation, the same spectrum always appears. In other words, the luminescence of uranyl salts is a phenomenon of true fluorescence, not of resonance. This obviously demands that the transition to the ground state should be from a single electronic level in the excited state. Whatever may be the absorbed energy, the surplus vibrational energy must be lost by some internal mechanism (e.g., collisions, etc.) and the excited molecule must fall to the upper electronic level before luminescence can occur. In Van Heel's scheme, however, the electronic frequency is 20383 cm. [-1], while bands are shown to arise from several vibrational levels extending up to 22554 cm. [-1] above the ground state, i.e., up to 2171 cm.[-1] above the excited electronic state. In the absorption spectrum at − 185° C. also, bands arise from levels as high as 2577 cm.[-1] above the ground level. Thus, it is easily seen that the scheme is quite unsatisfactory.

A7

3. Basis for the New Analysis

In spite of the emitter being the same, minor variations in the spectra of various uranyl salts, undoubtedly due to the interaction of the crystal-line fields, are observed. It is, however, necessary to have a common inter-pretation for all the spectra, slight modifications of which would be sufficient to satisfy the more complicated cases. The interpretation has to be consistent with the observational fact mentioned above which imposes the strict condition that the bands should arise out of a single (if more, they should be closely spaced) electronic level in the upper state. With this restriction and the unavoidable lack of knowledge of the energy states of free UO_2^{++} molecule, the problem becomes more complicated. Any useful information for further progress can, only be had from a co-ordinated study of the fluorescence and the absorption spectra, although the Raman and the infra-red spectral data should also be of great help. Taking for example, the fluorescence and the absorption spectra of uranyl fluoride II at $-185°$ C., it is observed (previous paper) that the first two bands designated as A and B in the fluorescence spectrum appear also in
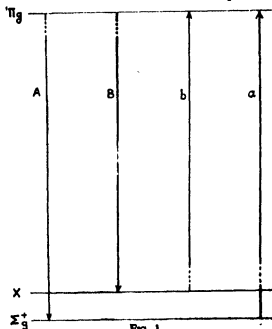
Fig. 1

absorption (named a and b) with the important difference that while in fluo-rescence B is far stronger than A, in absorption a is stronger than b. This fact naturally leads to the suggestion that the three levels which give rise to these bands are situated as shown in Fig. 1. (It should be mentioned,

however, that Σg — X interval is only 150 cm.$^{-1}$]. The names given to
the levels may be taken to be arbitrary for the present.) It requires that
$^1\Sigma g$ — $^1\Pi g$ transition is forbidden while $^1\Pi g$ — X is allowed. In absorption,
at low temperatures, due to the prohibitive Boltzmann factor, the X level
will be very much less populated than the $^1\Sigma g$ level with the result that
in spite of the higher X — $^1\Pi g$ transition probability, the *a* band will be
stronger than the *b* band.

4. INTERPRETATION OF THE FLUORESCENCE SPECTRA

(a) Simpler Cases

Uranyl fluoride II.—The three frequencies of the UO_2^{++} molecule are
known from the Raman and the infra-red spectral studies. The sym-
metric valence frequency $\nu_1 = 860$ cm.$^{-1}$, the deformational frequency
$\nu_2 = 210$ cm.$^{-1}$ and the anti-symmetric valence frequency $\nu_3 = 930$ cm.$^{-1}$.
The A–B (or Σg – X) interval of 150 cm.$^{-1}$ does not represent any of these
known vibrational frequencies, hence our assumption that both Σg and X
are electronic levels. The average A–C interval = 230 cm.$^{-1}$ The pre-
sence of the E band is very doubtful for several reasons, but if it is present
B–E interval = 247 cm.$^{-1}$ These intervals indeed represent the ν_2 frequen-
cy. The intervals such as A–A, B–B and C–C which are nearly equal
have an average value of 863 cm.$^{-1}$ This is due to the symmetric valence
frequency ν_1. The several bands of the spectrum can now be interpreted
as in Table I.

TABLE I

Int.	Desig.	ν Obs.	ν Cal.	Assignment	Remarks
0	A	20234	20232	A_0	Electronic frequency
8	B	20082	20082	B_0	Do
2	A	19366	19369	$A_0 - \nu_1$	
10	B	19217	19219	$B_0 - \nu_1$	Group II
4	C	19137	19139	$A_0 - \nu_1 - \nu_2$	Average
0 ?	E	18970 ?	18972	$B_0 - \nu_1 - \nu_2$	
1	A	18504	18506	$A_0 - 2\nu_1$	
9	B	18353	18356	$B_0 - 2\nu_1$	Group III
4	C	18276	18276	$C_0 - 2\nu_1 - \nu_2$	Average
0	A	17641	17643	$A_0 - 3\nu_1$	
4	B	17492	17493	$B_0 - 3\nu_1$	Group IV
4	C	17415	17413	$A_0 - 3\nu_1 - \nu_2$	Average
0	B	16640	16630	$B_0 - 4\nu_1$	Visually estimated
0	C	16577	16550	$A_0 - 4\nu_1 - \nu_2$	Do

D. D. Pant

Autunite.—The spectrum has been studied by Van Heel. He has also suggested an analysis for it. But the analysis again suffers from the same defects. We give in Table II the analysis of the bands on the same basis as above. A–B = 114 cm.$^{-1}$, ν_2 = 218 cm.$^{-1}$ and ν_1 = 820 cm.$^{-1}$ The spectrum extends only up to the 4th group, and the data do not appear to be complete.

TABLE II

Int.	Desig.	ν Obs	ν Cal	Assignment	Remarks
	A		19962	A_0	Not observed
5	B	19848	19848	B_0	
	C		19744	$A_0 - \nu_2$	Do
1	F	19629	19620	$B_0 - \nu_2$	Group I
1	F	19515	19426	$A_0 - 2\nu_2$	
1	G	19400	19402	$B_0 - 2\nu_2$	
5	B	19028	19028	$B_0 - \nu_1$	
3	C	18929	18924	$A_0 - \nu_1 - \nu_2$	
1	E	18830	18810	$B_0 - \nu_1 - \nu_2$	Group II
1	F	18714	18706	$A_0 - \nu_1 - 2\nu_2$	
1	G	18586	18592	$B_0 - \nu_1 - 2\nu_2$	
5	B	18206	18208	$B_0 - 2\nu_1$	
3	C	18098	18104	$A_0 - 2\nu_1 - \nu_2$	
1	E	18006	17990	$B_0 - 2\nu_1 - \nu_2$	Group III
1	F	17901	17986	$A_0 - 2\nu_1 - 2\nu_2$	
1	G	17784	17772	$B_0 - 2\nu_1 - 2\nu_2$	
2	B	17388	17388	$B_0 - 3\nu_1$	Group IV

(b) More Complicated Cases

The spectral analysis becomes more complicated if in addition to the A, B, C and E bands the D bands also appear. Since the A–C and B–E intervals are equal to the deformational frequency, the position of the D bands between C and E becomes difficult to explain as neither the A–D nor the B–D interval corresponds to any of the three known vibrational frequencies of the UO_2^{++} molecule.* Although most of the series, namely, A, B, C, E, F, G, H, I, K and L could be explained in a manner as given above, the D bands cannot be ignored. Arbitrarily explaining the frequencies without regard to the peculiar behaviour of these bands, would have no meaning. We have seen already the unstable nature of these bands in the uranyl chloride spectrum. They appear only at — 185° C. and disappear even at temperatures as low as — 110° C. They are accompanied by extended diffuseness, lose their discrete character easily and can be made

---

* A frequency close to the ν_2 frequency observed by Satyanarayana in the Raman spectrum of the solution of uranyl chloride, however, does correspond to the B–D. interval,

to appear as short continua. It is evident that the D bands should have their origin in an unstable state, unlike the other bands. A satisfactory explanation cannot be given before the several possibilities which could give rise to such characteristics are fully discussed. In the following, therefore, we give the analysis for the spectra of the uranyl sulphate, the acetate, the nitrate, the chloride, fluoride II and uranyl potassium sulphate without proposing a definite assignment for the D bands.

TABLE III

Int.	Desig.	ν Obs.	ν Cal.	Assignment	Remarks
m	A	20494	20496	A_0	
s	B	20332	20332	B_0	
d	C	20245	20238	$A_0 - \nu_2$	
$v\,d$	D	20139	20149	D_0	
$v\,d$	E	20071	20074	$B_0 - \nu_2$	Group I
m	F	19978	19980	$A_0 - 2\nu_2$	
d	F'	19887	19891	$D_0 - \nu_2$	
d	G	19786	19816	$B_0 - 2\nu_2$	
d	H	19714	19722	$A_0 - 3\nu_2$	
d	A	19637	19639	$A_0 - \nu_1$	
s	B	19469	19475	$B_0 - \nu_1$	
m	C	19383	19381	$A_0 - \nu_1 - \nu_2$	
d	D	19292	19294	$D_0 - \nu_1$	
d	E	19218	19219	$B_0 - \nu_1 - \nu_2$	Group II
$v\,d$	F	19122	19123	$A_0 - \nu_1 - 2\nu_2$	
d	F'	19021	19036	$D_0 - \nu_1 - \nu_2$	
$v\,d$	G	18934	18959	$B_0 - \nu_1 - 2\nu_2$	
$v\,d$	H	18869	18865	$A_0 - \nu_1 - 3\nu_2$	
$v\,d$	A	18792	18782	$A_0 - 2\nu_1$	
s	B	18620	18618	$B_0 - 2\nu_1$	
m	C	18534	18524	$A_0 - 2\nu_1 - \nu_2$	
$v\,d$	D	18435	18435	$D_0 - 2\nu_1$	
d	E	18344	18360	$B_0 - 2\nu_1 - \nu_2$	Group III
$v\,d.$	F	18250	18269	$A_0 - 2\nu_1 - 2\nu_2$	
d	F'	18160	18177	$D_0 - 2\nu_1 - \nu_2$	
d	G	18065	18102	$B_0 - 2\nu_1 - 2\nu_2$	
$v.d.$	H	18010	18011	$A_0 - 2\nu_1 - 3\nu_2$	
$v.d.$	A	17935	17925	$A_0 - 3\nu_1$	
m	B	17757	17761	$B_0 - 3\nu_1$	
m	C	17672	17667	$A_0 - 3\nu_1 - \nu_2$	
d	D	17582	17578	$D_0 - 3\nu_1$	Group IV
d	E	17490	17503	$B_0 - 3\nu_1 - \nu_2$	
d	F	17418	17409	$A_0 - 3\nu_1 - 2\nu_2$	
$v.d.$	H	17157	17151	$A_0 - 3\nu_1 - 3\nu_2$	
$v\,d$	A	17068	17068	$A_0 - 4\nu_1$	
$v.d.$	B	16904	16905	$B_0 - 4\nu_1$	
d	C	16825	16821	$A_0 - 4\nu_1 - \nu_2$	Group V
$v\,d.$	D	16729	16721	$D_0 - 4\nu_1$	
d	E	16637	16647	$B_0 - 4\nu_1 - \nu_2$	
$v.d.$	F	16535	16553	$A_0 - 4\nu_1 - 2\nu_2$	
d	B	16065	16048	$B_0 - 5\nu_1$	Group VI
d	C	15985	15964	$A_0 - 5\nu_1 - \nu_2$	

D. D. Pant

URANYL SULPHATE

We have A–B = 165 cm.$^{-1}$, B–D = 183 cm.$^{-1}$, $\nu_2 = 258$ cm.$^{-1}$ and $\nu_1 = 857$ cm.$^{-1}$

The λ values given by Nichols and Howes have been used after converting them into wave numbers The designations of the bands are our own. Similar bands in all the spectra have similar designations.

Uranyl Acetate

We have A–B = 150 cm.$^{-1}$ B–D = 150 cm.$^{-1}$, $\nu_1 = 855$ cm.$^{-1}$ and
$$\nu_2 = 235 \text{ cm.}^{-1}$$

TABLE IV

Int	Desig.	ν Obs	ν Cal	Assignment	Remarks
v.d	A	20728	20733	A_0	
m	B	20583	20583	B_0	
	C		20498	$A_0 - \nu_2$	
d	D	20436	20433	D_0	Group I
m	E	20349	20348	$B_0 - \nu_2$	
m	F	20278	20263	$A_0 - 2\nu_2$	
d	G	20148	20113	$B_0 - 2\nu_2$	
v d	A	19887	19878	$A_0 - \nu_1$	
v	B	19730	19728	$B_0 - \nu_1$	
m	C	19641	19643	$A_0 - \nu_1 - \nu_2$	
v d	D	19576	19578	$C_0 - \nu_1$	Group II
a	E	19488	19491	$B_0 - \nu_1 - \nu_2$	
d	F	19416	19408	$A_0 - \nu_1 - 2\nu_2$	
v d	G	19352	?	$B_0 - \nu_1 - 2\nu_2$	The observed G—G interval is 796 cm.$^{-1}$
v d	A	19013	19023	$A_0 - 2\nu_1$	
s	B	18863	18873	$B_0 - 2\nu_1$	
m	C	18785	18777	$A_0 - 2\nu_1 - \nu_2$	
v d	D	18714	18723	$D_0 - 2\nu_1$	Group III
d	E	18627	18635	$B_0 - 2\nu_1 - \nu_2$	
d	F	18565	18553	$A_0 - 2\nu_1 - 2\nu_2$	
v d	G	18376	18400	$B_0 - 2\nu_1 - 2\nu_2$	
v d	A	18164	18168	$A_0 - 3\nu_1$	
s	B	18013	18018	$B_0 - 3\nu_1$	
m	C	17932	17933	$A_0 - 3\nu_1 - \nu_2$	Group IV
v d.	E	17757	17783	$B_0 - 3\nu_1 - \nu_2$	
v.d	F	17700	17699	$A_0 - 3\nu_1 - 2\nu_2$	

In the last two groups only the B and C bands are present.

Uranyl Nitrate

The B, C, D and E bands (E, D, C, B bands of Nichols and Howes) of the spectrum of uranyl nitrate agree with the corresponding bands of the

above spectrum. No separate analysis is, therefore, given. There is a slight difference in the v_1 and v_2 frequencies and other intervals. Thus A–B = 167 cm.$^{-1}$, B–D = 165 cm.$^{-1}$, $v_2 = 250$ cm.$^{-1}$ and $v_1 = 859$ cm.$^{-1}$

Uranyl Chloride

The peculiarity of the D bands in this spectrum is that they continuously shift towards the B band in the successive groups A–D interval in the first group = 196 cm.$^{-1}$, but in the 4th group it has already fallen to 72 cm.$^{-1}$ The D–D interval is, however, constant and is equal to 854 cm^{-1} B–B or C–C or E–E intervals are equal to 876 cm^{-1} We have, therefore, $v_1 = 854$ cm.$^{-1}$ and 876 cm.$^{-1}$, $v_2 = 246$ cm.$^{-1}$ A–B = 174 cm.$^{-1}$

TABLE V

Int.	Desig.	v Obs.	v Cal	Assignment	Remarks
..	A	..	20709	A_0	
9	B	20535	20535	B_0	
1	C	20462	20463	$A_0 - v_2$	
6	D	20339	20339	D_0	
8	E	20286	20289	$B_0 - v_2$	
1	F	20130	20117	$A_0 - 2v_2$	
2	F′	20093	20093	$D_0 - v_2$	
1	G	20051	20043	$B_0 - 2v_2$	
1	H	19882	19871	$A_0 - 3v_2$	
1	A	19833	19833	$A_0 - v_1$	
10	B	19655	19659	$B_0 - v_1$	Other weaker bands are
6	C	19574	19577	$A_0 - v_1 - v_2$	masked by the general
6	D	19489	19495	$D_0 - v_1$	diffuseness
6	E	19405	19413	$B_0 - v_1 - v_2$	

Other bands in the higher groups can also be similarly explained.

Uranyl Fluoride I

In this spectrum both the C and the D bands shift apart in the successive groups. As above, although the B–C and the B–D intervals considerably change, the B–B, the C–C and the D–D intervals are constant but different. This gives the v_1 frequency to be 819 cm.$^{-1}$, 827 cm^{-1} and 795 cm.$^{-1}$ respectively. $v_2 = 176$ cm.$^{-1}$

118

D. D. Pant

TABLE VI

Int.	Desig.	ν Obs.	ν Cal.	Assignment	Remarks
	A		20188	A_0	
6	B	20095	20095	B_0	
10	C	20012	20012	$A_0 - \nu_2$	
3	D	19967	19967	D_0	
4	F	19912	19919	$B_0 - \nu_2$	
	F		19836	$A_0 - 2\nu_2$	
0	F'	19794	19791	$D_0 - \nu_2$	
3	G	19728	19743	$B_0 - 2\nu_2$	
1	H	19661	19666	$A_0 - 3\nu_2$	
3	I	19578	19567	$B_0 - 3\nu_2$	
10	B	19274	19276	$B_0 - \nu_1$	
12	C	19183	19185	$\left. \begin{array}{l} A_0 - \nu_1 - \nu_2 \\ D_0 - \nu_1 \end{array} \right\}$	Coincide
	D	19173	19172		
8	E	19112	19100	$B_0 - \nu_1 - \nu_2$	
1	F	19028	19009	$A_0 - \nu_1 - 2\nu_2$	
3	H	18846	18833	$A_0 - \nu_1 - 3\nu_2$	
3	I	18718	18748	$B_0 - \nu_1 - 3\nu_2$	
1	A	18521	18534	$A_0 - 2\nu_1$	
8	B	18455	18457	$B_0 - 2\nu_1$	
3	D	18·90	18377	$D_0 - 2\nu_1$	The order of C and D is
10	C	18345	18358	$A_0 - 2\nu_1 - \nu_2$	reversed. With the D
8	E	18286	18281	$B_0 - 2\nu_1 - \nu_2$	band diffuseness starts
1	F'	18198	18201	$D_0 - 2\nu_1 - \nu_2$	End of the diffuseness
1	G	18066	18105?	$B_0 - 2\nu_1 - 2\nu_2$	
2	I	17923	17929	$B_0 - 2\nu_1 - 3\nu_2$	
0	A	17686	17609	$A_0 - 3\nu_1$	
5	B	17636	17638	$B_0 - 3\nu_1$	
3	D	17573	17582	$D_0 - 3\nu_1$	Beginning of diffuseness
10	C	17523	17533	$A_0 - 3\nu_1 - \nu_2$	
8	E	17457	17462	$B_0 - 3\nu_1 - \nu_2$	
1	F'	17399	17406	$D_0 - 3\nu_1 - \nu_2$	End of diffuseness
1	I	17085	17110	$B_0 - 3\nu_1 - 3\nu_2$	

The rest of the bands belonging to the higher groups can similarly be explained.

Uranyl Potassium Sulphate

We have A–B = 90 cm.$^{-1}$, B–D = 120 cm.$^{-1}$, ν_1 = 833 cm.$^{-1}$ and ν_2 = 172 cm.$^{-1}$ The spectrum contains a large number of bands which have been measured by Nichols and Howes.

TABLE VII

Int.	Desig.	ν Obs	ν Cal.	Assignment	Remarks
νd	A	20475	20475	A_0	
m	B	20385	20385	B_0	
d	C	20313	20303	$A_0 - \nu_2$	
m	D	20265	20265	D_0	
m	E	20197	20213	$B_0 - \nu_2$	
s	F	20109	$\left.\begin{array}{c}20131\\20093\end{array}\right\}$	$\left.\begin{array}{c}A_0 - 2\nu_2\\D_0 - \nu_2\end{array}\right\}$	The two have probably coincided
νd	G	20047	20041	$B_0 - 2\nu_2$	
d	H	19973	19959	$A_0 - 3\nu_2$	
m	J	19910	19021	$D_0 - 2\nu_2$	
d	K	19786	19782	$A_0 - 4\nu_2$	
d	L	19726	19697	$B_0 - 4\nu_2$	
m	A	19634	19642	$A_0 - \nu_1$	
s	B	19554	19552	$B_0 - \nu_1$	
m	C	19467	19470	$A_0 - \nu_1 - \nu_2$	
m	D	19440	19432	$D_0 - \nu_1$	
d	E	19365	19380	$B_0 - \nu_1 - \nu_2$	
m	F	19272	$\left.\begin{array}{c}19298\\19260\end{array}\right\}$	$\left.\begin{array}{c}A_{0-1} - 2\nu_2\\D_0 - \nu_1 - \nu_2\end{array}\right\}$	
$\nu d.$	G	19234	19208	$B_0 - \nu_1 - 2\nu_2$	
d	H	19134	19122	$A_0 - \nu_1 - 3\nu_2$	
νd	J	19084	19088	$D_0 - \nu_1 - 2\nu_2$	
νd	K	18952	18950	$A_0 - \nu_1 - 4\nu_2$	
νd	L	18886	18864	$B_0 - \nu_1 - 4\nu_2$	

The other groups can be explained in a similar way. It will, however, be mentioned here that in the last three groups there are no D, F or J bands while A, B, C, F, G, H are present.

5. DISCUSSION

It is known from the study of the molecular spectra that the iso-electronic molecules are similar in many respects. The 16 electron molecules, for example, CO_2, CS_2, $HgCl_2$, etc., all have the closed configuration $\sigma_g^2 \; \sigma_u^2 \; \sigma_g^2 \; \sigma_u^2 \; \pi_u^4 \; \pi_g^4$ and have a $^1\Sigma_g^+$ ground state. They are all, without exception, linear molecules belonging to the $D \infty h$ symmetry. The UO_2^{++} molecule has also 16 electrons, namely, the four $5 d$ bonding electrons of the U^{++} ion (configuration $5 s^2 \; 5 p^6 \; 5 d^4$) and 12 sp bonding and non-bonding electrons of the two oxygen atoms. The X-ray analysis of Fan-kuchen (1936) shows that the molecule is linear. Conn and Wu, however, suggest a bent structure for it, primarily on the basis of the appearance of the ν_2 frequency in the Raman spectra of the solutions of uranyl salts. How-ever the UO_2^{++} may still be linear in the solid state, as the strong infra-red absorption of the ν_3 frequency appears to show. The closed configuration of the molecule will have $^1\Sigma^+ g$ ground state. Definite magnetic data are

lacking to test this point, although uranyl nitrate is reported to be diamagnetic in confirmation with the suggestion.* The next state (X) cannot be due to spin and may be a separate level altogether. The excited state may be a $(\pi^{-1}g)$ og, $^1\Pi g$ state as observed in other similar molecules (Mulliken, 1941). The $^1\Pi g$–$^1\Sigma g$ transition would then be forbidden, as already observed. The transition to the X state is probably allowed or is at least more favoured.

Now, both in crystals (Van Vleck, 1937) and in polyatomic molecules (Sponer, 1941), the violation of selection rules is of a frequent occurrence. A forbidden transition can be made allowed by the excitation of a non-totally symmetric vibration. (An allowed transition in the neighbourhood and the effect of the crystalline field would also increase the probability of the transition.) The vibrational structure of such a transition, however, differs in a characteristic way from that of an allowed transition. In the forbidden transition, there must occur a change of a non-totally symmetrical vibration by at least one quantum number upon which will then be superposed the changes of a totally symmetrical vibration. In such a transition the (0, 0) band should be either absent or should be very weak. The weak intensity of the (0, 0) band, i.e., A band of the first group and of the A series which is a pure v_1 progression is readily understood. The high intensity of the C bands which are due to a (0, 1) transition of a non-totally symmetric v_2 vibration (UO_2^{++} being assumed to be linear) upon which the changes of the totally symmetric vibration v_1 are superposed is again clear. The A and the D series in our spectra closely resemble the I and the A series of the fluorescence spectrum of solid benzene (Kronenberger, 1930). The analysis of Sponer and others of these bands is also exactly the same as ours for the A and the C bands. The increase in the intensity of the C bands after at least one quantum of v_1 is superposed on the (0, 1) v_2 transition also agrees with the observations of the spectrum of benzene.

The vibrational structure of the $^1\Pi g \rightarrow$ X transition agrees well with an allowed transition. The (0, 0) band should be strong and the totally symmetrical vibration should be the only one to change by any quantum number so as to give rise to strong bands. The strong B series which is a pure v_1 progression is what should be expected. The B and the D are the only two series which appear with high intensity in all the spectra studied. The intensities of the other series, however, greatly vary from spectrum to spectrum. Such cases must be attributed to the effect of the crystalline field. The general increase in the intensity of the bands in the second

group denotes the slight relative displacement of the positions of the energy minima in the ground and the excited states.

The shifting of the C bands in the fluoride I spectrum finds a natural explanation in our scheme, *i.e.*, it is due to the v_1 frequency being slightly different for the molecule in the $^1\Sigma g$ and X states. If the B–C interval were due to a vibrational frequency, a strong coupling between this vibration and v_1 would have been necessary to explain the shifting. Similar remarks may also apply to the D bands.

In conclusion, the author wishes to thank Sir C. V. Raman for helpful discussions.

SUMMARY

From some direct experimental evidence, it is concluded that the entire fluorescence spectrum of the uranyl salts arises out of a transition from a single excited state (designated $^1\Pi g$) to the several vibrational states of two close ground levels (designated $^1\Sigma g$ and X) and that the $^1\Pi g \rightarrow ^1\Sigma g$ transition is much less favoured than the $^1\Pi g$–X transition. The v_1 and v_2 frequencies taking part in the transition agree with those observed in the Raman and infra-red spectra; v_1 is, however, very much more prominent. The vibrational structure of the $^1\Pi g$–$^1\Sigma g$ transition resembles that of a forbidden transition, while the structure of the other is that of an allowed one. The intensity distribution of the A, B and C bands is explained. No specific explanation of the D bands is given. Van Heel's analysis is shown to be unsatisfactory.

REFERENCES

1. Conn and Wu		*Trans Farad Soc*, 1938, **34**, 1483
2. Fankuchen	.	*Z Krist*, A, 1935, **91**, 473 . 1936, **94**, 2212.
3. Dieke and Van Heel	..	*Leiden Communications*, 1925, Suppl No. 55 A.
4 Van Heel	.	*Ibid*, Suppl No. 55 B
5. Mulliken	..	*Phys Rev*, 1941, **60**, 506.
6. Nichols and Howes	..	*Fluorescence of Uranyl Salts*, Carnegie Institute Publication, 1919, No 298
7. Pringsheim		*Handbuch der Physik*, 1933, **23**/1
8. Satyanarayana	..	*Proc. Ind Acad Sci*, 1942, **15**, 414.
9. Sponer	.	*Rev. Mod Phys*, 1941, **13**, 1941.
10. Kronenberger	.	*Z. f Phys*, 1930, **63**, 494
11. Van Vleck	..	*J Phy. Chem*, 1937, **41**, 67.

COEFFICIENT OF ASSOCIATION BETWEEN TWO ATTRIBUTES IN STATISTICS

By M. LAKSHMANAMURTI

(Andhra University, Guntur)

THE object of this paper is to study association between two attributes given in a 2×2 table and to introduce a suitable coefficient of association. Yule's coefficient of association Q in Prof. Yule's own words, " is the simplest available, though not the most advantageous. For moderate association this coefficient gives much the larger values." I have introduced the notion of measures of association, indicators of association and proposed a suitable coefficient of association. For a number of standard examples I have calculated all these constants.

NOTATION EMPLOYED

A and B are the attributes the association between which is studied. Not A's and not B's are represented by α and β; the frequencies are represented by a, b, c and d as shown in the table.

	A	a	
B	a	b	$a + b$
β	c	d	$c + d$
	$a + c$	$b + d$	N

p' and p'' represent the probabilities of B being in the universe of A and α respectively; q' and q'', the probabilities of A being in the universe of B and β respectively; so that

$$p' = \frac{a}{a+c}, \ p'' = \frac{b}{b+d}; \ q' = \frac{a}{a+b}, \ q'' = \frac{c}{c+d}$$

$p' > p''$ implies association between A and B, $p' > p''$ implies disassociation between A and B. In what follows I shall treat association only, for disassociation between A and B is association between A and β and we need only interchange the two rows. Strength of association is usually judged by the difference $p = p' - p''$. (In Ex. 6, mother's habits and father's habits, $p = \cdot 8622 - \cdot 1234 = \cdot 7388$.) Whether this difference is significant is judged by the value p/σ_p (which in this case is 42·5. In Ex. 7, deaf-mutism and

imbecility $p = \cdot 009228 - \cdot 00056 = \cdot 0086$ which looks to be very small but p/σ_p is now 66·11. Thus the mere difference, p cannot indicate intensity of association.) The difference $q = q' - q''$ has an equal claim to indicate association between A and B. We can judge the significance of q by considering q/σ_q.

If with the object of forming a coefficient of association, the geometric mean of p and q be formed we get $r = \sqrt{pq}$ and expressing this in terms of the frequencies, we obtain the familiar expression,

$$r = \frac{(ad - bc)}{\sqrt{(a+b)\,(c+d)\,(a+c)\,(b+d)}} \cdot *$$

This expression gives the coefficient of correlation as calculated from a 2×2 table. Incidentally we deduce that $\chi^2 = Npq$. The relation $r = \sqrt{pq}$ shows the connection between association and correlation. For very asymmetrical tables r is very small. In Ex. 7, $r = \cdot 0156$. When r is small, the correlation ratio is calculated to see if it is sensibly larger than r. In this case, however, that is for a 2×2 table both the correlation ratios are equal to r. Thus r is not suitable as a coefficient of association except for tables which are fairly symmetrical.

A unified method of approach may be suggested by proposing a coefficient

$$\phi = \mathrm{F}\,(a, b, c, d)$$

where F is a function of degree zero in a, b, c, d and such that

$$= + 1 \quad \text{when } b = c = 0$$
$$= - 1 \quad \text{when } a = d = 0$$
$$= \ \ 0 \quad \text{when } ad = bc.$$

Of this form are, p or q, r, Yule's coefficient Q, and the coefficient $\wedge$ that I am proposing in this paper. The variance of ϕ is a function of four unknowns a, b, c and d. From out of the ϕ's satisfying the above conditions, a selection cannot be made directly of those that have the smallest standard errors. I shall therefore be content with showing that in most cases the S.E. of $\wedge$ is less than that of Q.

Instead of measuring intensity of association by the difference p, I propose that it be measured by the ratio $\dfrac{p'}{p''}$. I designate this ratio by M_1 and call it a measure of association. This indicates that the proportion of B's in the universe of A's is M_1 times the proportion of B's in the

---

* See 13·25, page 252, Yule and Kendall, *Theory of Statistics*.

universe of a's. (In Ex. 6, $M_1 = 6 \cdot 987$ and in Ex. 7 it is $20 \cdot 24$.) $M_2 = \dfrac{q'}{q''}$
is another measure of association based on the proportions A's in the universe
of B's and in the universe of β's. $M = \frac{1}{2}(M_1 + M_2)$ is the mean measure of
association based on the proportions of A's and B's in the above noted
universes. M_1, M_2 and M have the property that they vary from 1 at
independence to ∞ at complete association. I define the first indicator of
association $\lambda = 1 - \dfrac{1}{M}$ which varies from 0 at independence to 1 when there
is complete association $(A\beta) = 0$ or $(\alpha B) = 0$. When there is disassociation
between A and B, $(p' < p'')$, I consider association between A and β,
calculate λ and attach a negative sign to it and that will be the first
indicator of disassociation between A and B. λ may be treated as a
coefficient of association between A and B, but λ is based on the proportions
of A's and B's only in universes of B and β and A and α. The association
between A and B must be the same as the association between α and β.

$$\frac{\text{The proportion of } \beta\text{'s in the universe of } \alpha\text{'s}}{\text{The proportion of } \beta\text{'s in the universe of A's}} = \frac{1 - p''}{1 - p'} = M_1'.$$

I shall call the measure of association based on these proportions only.

$$\frac{\text{The proportion of } \alpha\text{'s in the universe of } \beta\text{'s}}{\text{The proportion of } \alpha\text{'s in the universe of B's}} = \frac{1 - q''}{1 - q'} = M_2'$$

is the measure of association based on these proportions.

$M' = \frac{1}{2}(M_1' + M_2')$ is the mean measure of association suggested by the
proportions of α's and β's. $\lambda' = 1 - \dfrac{1}{M'}$ is the second indicator of associ-
ation. $\Lambda = \frac{1}{2}(\lambda + \lambda')$ is the mean coefficient of association or simply the
coefficient of association between the attributes.

I shall now express the indicators in terms of the fundamental
quantities p', p'', q', q''. $M_1 = \dfrac{p'}{p''}$, $M_2 = \dfrac{q'}{q''}$.

$$M = \frac{p'q'' + p''q'}{2\,p''q''}, \quad \lambda_1 = \frac{p' - p''}{p'}, \quad \lambda_2 = \frac{q' - q''}{q'}$$

$$\lambda = \frac{p'q'' + p''p'' - 2\,p''q''}{p'q'' + p''q'}$$

$$= \frac{q''\,(p' - p'') + p''\,(q' - q'')}{p'q'' + p''q'}$$

$$= \frac{M_1\lambda_1 + M_2\lambda_2}{M_1 + M_2}$$

which shows that λ is the weighted arithmetic mean of λ_1 and λ_2.

Yule's coefficient, $Q = \dfrac{ad - bc}{ad + bc}$

$$= \dfrac{\dfrac{a}{a+c}\dfrac{d}{b+d} - \dfrac{b}{b+d}\dfrac{c}{a+c}}{\dfrac{a}{a+c}\dfrac{d}{b+d} + \dfrac{b}{b+d}\dfrac{c}{a+c}} = \dfrac{p'(1-p'') - p''(1-p')}{p'(1-p'') + p''(1-p')}$$

$$= \dfrac{p' - p''}{p' + p'' - 2\,p'p''}$$

Q can also be expressed as $\dfrac{q' - q''}{q' + q'' - 2\,q'q''}$.

We shall now obtain a relation between the four measures M_1, M_2, M_1', M_2'.

$$1 - Q = \dfrac{2\,p''(1-p')}{p''(1-p') + p'(1-p'')} = \dfrac{2}{1 + M_1 M_1'}$$

Similarly $\quad 1 - Q = \dfrac{2}{1 + M_2 M_2'}$, so that $M_1 M_1' = M_2 M_2'$.

We shall now show that $\wedge < Q$.

$$1 - \wedge = \dfrac{1}{M_1 + M_2} + \dfrac{1}{M_1' + M_2'}$$

$1 - \wedge > 1 - Q$ if $\tfrac{1}{2}(1 + M_1 M_1')(M_1 + M_2 + M_1' + M_2')$

$$> (M_1 + M_2)(M_1' + M_2')$$

From $M_1 M_1' = M_2 M_2'$ we have

$$\dfrac{M_1}{M_1 + M_2} = \dfrac{M_2'}{M_1' + M_2'}$$

and using this, the above inequality gives,

$$\tfrac{1}{2}(1 + M_1 M_1')(M_1 + M_2') > M_1 M_2'$$

i.e., $\quad M_1 + M_2' + M_1{}^2 M_1' + M_1 M_1' M_2' < 2\,M_1 M_2'$

i.e., $\quad M_1 + M_2' + M_1(M_1 M_1' - M_2') + M_1 M_2'(M_1' - 1) > 0$

i.e., $\quad M_1 + M_2' + M_1 M_2'(M_1 - 1) + M_1 M_1'(M_1' - 1) > 0$

which is true.

VARIANCE OF Q

Following the method suggested by R. A. Fisher on page 302 of his book (*Statistical Methods for Research Workers*, 7th edition), the variance of Q is $\vee (Q) = \left(\dfrac{1 - Q^2}{2}\right)^2 \cdot T$

where
$$T = \frac{1}{a} + \frac{1}{b} + \frac{1}{c} + \frac{1}{d}$$

$$= 1 - \frac{1}{2M} - \frac{1}{2M'}, \text{ and } M = \frac{a(b+d)}{b(a+c)} + \frac{a(c+d)}{c(a+d)} \text{ and } M' = \cdots$$

$$\frac{\partial \wedge}{\partial a} = + \frac{1}{2M^2} \frac{\partial M}{\partial a} + \frac{1}{2M'^2} \frac{\partial M'}{\partial a}$$

$$= \frac{1}{4M^2}\left(\frac{\partial M_1}{\partial a} + \frac{\partial M_2}{\partial a}\right) + \frac{1}{4M'^2}\left(\frac{\partial M_1'}{\partial a} + \frac{\partial M_2'}{\partial a}\right)$$

$$= \frac{1}{4M^2}\left(\frac{b+d}{b}\cdot\frac{c}{(a+c)^2} + \frac{c+d}{c}\cdot\frac{b}{(a+b)^2}\right)$$

$$+ \frac{1}{4M'^2}\left\{\frac{d}{c(b+d)} + \frac{d}{b(c+d)}\right\}$$

$$4a\,\frac{\partial \wedge}{\partial a} = \frac{1}{M^2}\left\{\frac{p'(1-p')}{p''} + \frac{q'(1-q')}{q''}\right\} + \frac{1}{M'^2}\left\{\frac{p'(1-p'')}{1-p'} + \frac{q'(1-q'')}{1-q'}\right\}$$

$$= \frac{(1-p')\,M_1 + (1-q')\,M_2}{M^2} + \frac{p''M_1' + q''M_2'}{M'^2}$$

Similarly,

$$-4b\,\frac{\partial \wedge}{\partial b} = \frac{(1-p')\,M_1 + (1-q')\,M_2}{M^2} + \frac{p''M_1' + q''M_2'}{M'^2}$$

$$-4c\,\frac{\partial \wedge}{\partial c} = \frac{(1-p')\,M_1 + (1-q')\,M_2}{M^2} + \frac{p''M_1' + q''M_2'}{M'^2}$$

$$4d\,\frac{\partial \wedge}{\partial d} = \frac{(1-p')\,M_1 + (1-q')\,M_2}{M^2} + \frac{p''M_1' + q''M_2'}{M'^2}.$$

If the quantities on the right-hand side of the four equations be designated by A, B, C, D,

$$a\left(\frac{\partial \wedge}{\partial a}\right)^2 = \frac{1}{16}\frac{A^2}{a}$$

and so,

$$\vee(\wedge) = \frac{1}{16}\left(\frac{A^2}{a} + \frac{B^2}{b} + \frac{C^2}{c} + \frac{D^2}{d}\right)$$

Since $\vee(Q) = \frac{1}{4}(1-Q^2)^2\,T$, we can assert that $\vee(\wedge) < \vee(Q)$ if A, B, C and D be each $< 2(1-Q^2)$.

In almost all the tables that I have given in this paper, $\wedge$ has a small by variance than Q. In Ex. 2 and Ex. 3 alone, the variance of $\wedge$ is greater than that of Q. Consider the following example from Palin Elderton's *Frequency Curves and Correlation* (3rd Ed., p. 170).

Strength to resist small-pox when attacked

	Recovered	Died	
Present ..	3,951	200	4,151
Absent ..	278	274	552
	4,229	474	4,703

$$p' = \cdot9344 \qquad M_1' = \frac{\cdot5781}{\cdot0656} = 8\cdot812$$
$$p'' = \cdot4219$$
$$q' = \cdot9519 \qquad M_2' = \frac{\cdot4963}{\cdot0481} = 10\cdot32$$
$$q'' = \cdot5036$$
$$M_1 = 2\cdot215 \qquad M' = 9\cdot566$$
$$M_2 = 1\cdot89 \qquad \lambda' = \cdot8955$$
$$\lambda = \cdot5128 \qquad \Lambda = \cdot7041,\ Q = \cdot8664$$

Tetrachloric r is ·7692 (Elderton, *ibid.*, p. 177).

$2(1-Q^2) = \cdot4988$. A < ·27, B < ·21, C < ·4, D < ·4, so that the S.E. of Λ is less than that of Q

$M_1 = 2\cdot215$ shows that the probability of vaccinated recovering is $2\cdot215$ times a vaccinated dying. $M_2 = 1\cdot89$ shows that the probability of recovered person being a vaccinated one is $1\cdot89$ times the probability of his being a non-vaccinated person. $M = 2\cdot0525$ is the mean measure based on these probabilities. $M_1' = 8\cdot812$ shows that the probability of a non-vaccinated person dying is $8\cdot812$ times his recovering. $M_2' = 10\cdot32$ shows that the probability of a non-vaccinated person is $10\cdot32$ times a vaccinated one dying. $M' = 9\cdot566$ is the mean measure based on these probabilities. Λ gives a correct idea of the intensity of association, based on these probabilities only. The calculation does not involve any assumptions regarding the nature of the universe. This coefficient is in better agreement with tetrachloric r than Q. Q gives too high a value.

I have calculated the several constants for the following examples and have given a tabular statement of the results.

Example 1.—(From the report of the Surgeon-General with Government of Madras.)

	First pregnancy	Not first pregnancy	
Still births	395	939	1,334
Not still births	3,811	10,444	14,255
	4,206	11,383	15,589

Example 2.—(From R. A. Fisher's *Statistical Methods for Research Workers,* 6th edition, p. 99.)

	Convicted	Not convicted	
Monozygotic twins .	10	3	13
Dizygotic twins . .	2	15	17
	12	18	30

Example 3.—

	Poor children per cent.	Well-to-do children per cent.	
Below normal weight ..	55	13	68
Above normal weight ..	11	48	59
	66	61	127

Example 4.—

	Father light eye colour	Father not light eye colour	
Son light eye colour .	471	148	619
Son not light eye colour ..	151	230	381

Example 5.—*Cholera inoculation and exemption from attack*

	Not attacked	Attacked	
Inoculated	276	3	279
Not inoculated	473	66	539
	749	69	818

Example 6.—*Mother's habits and Father's habits* (From *Tables for Biometrecians and Statisticians,* Karl Pearson)

	Mother's habits		
	Good	Bad	
Good	996	67	1,061
Bad	159	476	635
	1,153	543	1,696

Example 7.—Deaf-mutism and imbecility

	Imbeciles	Not imbeciles	
Deaf-mutes	451	14,795	15,246
Not deaf-mutes	48,425	32,465,329	32,512,754
	48,882	32,480,124	32,528,000

Examples 3, 4, 5 and 7 are from Yule and Kendall's *Theory of Statistics*.

The tables of Examples 2, 3, 4 and 6 are fairly symmetrical. and the value of r as calculated for the table with the formula $r = \sqrt{pq}$ should be fairly in agreement with a proposed coefficient of association.   A reference to the tabular statement below shows that $\wedge$ is consistent with the corresponding value of r while Q is far higher than r.

Example	1	2	3	4	5	6	7
λ ..	·107	·826	·758	·475	·7917	·814	·95
λ′ ..	·0196	·7731	·7724	·5933	·8458	·8904	·0195
∧	·063	·799	·7652	·534	·8188	·8522	·4848
Q ..	·072	·92	·897	·66	·85	·956	·91
r ..	·0179	·645	·62	·365	·1952	·712	0156

A glance at the above table shows that in all the examples, except the 7th, λ and λ′ are in agreement. The table of Ex. 5 is asymmetrical, yet the indicators are fairly in agreement. In Ex. 7 the indicators are far apart. I think the coefficient $\wedge$ = ·4848 describes more accurately the true association between deaf-mutism and imbecility than either ·95 or ·91. Apart from the face that as Prof. Yule points out Census data regarding deaf-mutes and imbeciles cannot be relied upon, the fact that the deaf-mutes claim in their universe almost the same percentage of not imbeciles as the not mutes do in theirs (these percentages being 97·04 and 99·85 respectively) cannot be ignored.   The difference, 2·81% is no doubt a significant difference its S.E. being ·137%. The data of the following example is not of the same kind as that of Ex. 7, but suggests why ·4848 represents better the degree of association than ·91 does.. The table is from page 480, *Biometrica*, Vol. 4.   The paper is concerning "Hereditary Deafness" the material being from E. A. Fay's *Marriages of the Deaf in America*.

		Father		
		Deaf	Hearing	
(Children)	Deaf	52	3,315	3,367
	Hearing .. .	383	7,179,796	7,180,179
		435	7,183,111	7,183,546

Tetrachloric $r = \cdot 58$ $\wedge = \cdot 5503$

$\lambda = \cdot 9931$ $Q = \cdot 9933$

$\lambda' = \cdot 1075$ $p = \cdot 11956$, its S E.$= \cdot 01678$.

I shall now examine how $\wedge$ behaves when the material of a known correlation table is grouped into four divisions and put as a 2×2 table. The table on p. 166 of Elderton's (*ibid*) is cut between 5 " heads " and 6 " heads " and the following table is reached (see p. 172 of the same book). The coefficient of correlation for the original table is $\cdot 5$.

Number of heads in second tossing	Number of heads second tossing		Number of heads in first tossing	
		0–5	6–10	
0– 5		15,330	5,086	20,416
6–10		5,086	7,266	12,352
		20,416	12,352	32,768

$\lambda = \cdot 4517$ $r = \cdot 34$ as calculated from this table

$\lambda' = \cdot 5765$ $Q = \cdot 6232$

$\wedge = \cdot 5141$ Tetrachloric, r is between $\cdot 51$ and $\cdot 52$.

From the correlation table of heights of fathers and sons (Prof. Karl Pearson's data) given in table 11·3 of Yule and Kendall's book, the following four tables are formed: —

TABLE I

Divided at the middle of $67'' \cdot 5 - 68'' \cdot 5$ for both statures

		Father short	Father tall	
Son short		340·5	111·25	451·75
Son tall		247·0	371·5	626·25
		587·5	482·75	1078

M. Lakshmanamurti

TABLE II

Divided at the end of 67″·5 for each stature

	Father short	Father tall	
Son short ..	269·5	95·75	365
Son tall . .	232·0	480·75	713
	501·5	576·5	1078

TABLE III

Divided at the end of 65″·5 for each stature

	Father short	Father tall	
Son short . ..	68	59·5	127·5
Son tall	154	797·5	951·5
	222	857	1078

TABLE IV

Divided at 63″·5 for each stature

	Father short	Father tall	
Son short .	7	20·5	27·5
Son tall . ..	58	992·5	1050·5
	65	1013	1078

The results are given in the following table:

	λ	λ'	Λ	Q
Table I . .	·5481	·5338	·5409	·6431
Table II	·6364	·5426	·5895	·7068
Table III	·7406	·4041	·5723	·7111
Table IV	·7986	·1548	·4767	·7086

Designating as usual the four frequencies by a, b, c, d as we go from Tables I to IV, a, b, c decrease and d increases. The classification short-short becomes purer in that really short fathers and short sons are grouped and the classification tall-tall becomes cruder in that the class includes not only the really tall-tall, but also tall-short, short-tall. This is reflected in the indicators λ and λ'. λ' decreases more rapidly than λ increases. $\wedge$ compares favourably with the true $r = \cdot 51$ of the original.

CONCLUSION

Although x^2 is available to examine if the departure from independence is significant, that test is designed to point out " the fact of significance, but does not measure the degree of association ".* The coefficient $\wedge$ is better designed to measure the degree of association than any other coefficient. Since $\wedge$ is less than Q, the defect that Q has namely of showing a high value for moderate association (see Ex. 4), is remedied in $\wedge$.

---

* R. A. Fisher, p. 94, *loc. cit.*

A NOTE ON THE PHLOBATANNINS OF KINO AND BUTEA GUMS

By G. V. KRISHNAMURTI AND T. R. SESHADRI

(From the Department of Chemistry, Andhra University)

DUE to the serious dearth of synthetic dye-stuffs during the past several years as a result of war, attention has been directed in India to the revival of plant dyes. There has been a number of cases, where materials, which contain predominantly phlobatannins, have been successfully used for dyeing. Among these the Kino and Butea gums seem to be the most important. The first is obtained from the trees of *Pterocarpus marsupium* and is also known as Malabar kino. The second is less frequently used and is obtained from the trees of *Butea frondosa*. Both plants belong to the same natural order, Leguminosæ. The above two gums have now been examined with a view to compare the phlobatannins present in them and also to obtain more information about this group of complex compounds.

Gum kino has been examined by several workers in the past, the most important contribution to our knowledge being that of Simonsen[1] in whose paper all previous work is conveniently summed up. He methylated and acetylated the kino directly. The kino methyl ether was obtained in the form of an almost colourless amorphous powder which did not melt below 300° and the acetyl compound was a brown amorphous powder. Analyses of these suggested the formula $C_{16}H_{11}O_4(OH)_4$ for the kino. It was considered to form a trimethyl ether and a triacetyl derivative. The molecular weight indicated that the molecule is at least twice that suggested by this formula. Fusion of the kino with potassium hydroxide yielded proto-catechuic acid and oxidation of the kino methyl ether with alkaline potassium permanganate gave veratric acid. These proved the presence of a catechol unit.

In view of the suggestion that phlobatannins have a 4-hydroxy-flavpinacol structure[2] it seemed to be desirable to obtain pure and colourless derivatives of these substances and see if they exhibit optical activity. The work done with this object in view is described in this note.

Kino and Butea gums have now been subjected to purification with a view to eliminate gummy matter and ether-soluble impurities. The purified

phlobatannins have been methylated and acetylated following in general the procedure of Simonsen. The methyl ethers and acetates are thereby obtained in an almost colourless condition. The former are amorphous powders ; the latter appear to be crystalline though the crystalline appearance is not definite. These substances exhibit marked optical activity thus providing support for the hydroxy-flavan structure for phlobatannins. The methyl ethers are quite stable to the action of aqueous hydrochloric acid whereas the parent phlobatannins quickly change under these conditions into insoluble phlobaphenes. This seems to indicate that the conversion requires the presence of free phenolic groups.

From the reactions and analytical results presented towards the end of the paper it appears that the phlobatannins of kino and Butea gums is identical. This is also supported by experiments on dyeing in which very similar results are obtained using the two gums.

EXPERIMENTAL

Purification of Kino gum.—Kino gum (10 g.) was dissolved in boiling water (100 c.c.) and the solution filtered. The clear cold filtrate was treated with saturated brine and the precipitated tannin (flesh coloured) was filtered, washed with brine solution and dried *in vacuo*   The dry solid was powdered and extracted with alcohol   Almost all of it went into solution. After distilling off as much alcohol as possible, the solution was treated with excess of ether. The flesh coloured precipitate was filtered and washed with ether. Further purification was affected by dissolving it again in alcohol and reprecipitating with ether. Thus water-soluble and ether-soluble impurities were removed. The ether solution contained small quantities of substances including probably catechin[3] and giving green colour with ferric chloride solution. But they were not further studied.

Methylation.—The purified kino (5 g.) was dissolved in alcohol (50 c.c.), dimethyl sulphate (5 c.c.) added and the mixture shaken well. To this caustic potash solution (3 g. in 3 c.c. water) was added in one lot and the mixture shaken vigorously. It became hot rapidly and the reaction had to be controlled by cooling under the tap. When it had subsided, the process was repeated using the same amount of dimethyl sulphate and potash. After shaking for about an hour the mixture was filtered and the clear solution was diluted with an equal amount of water. A pale brown amorphous solid separated out (yield, 2·5 g.). It was purified by repeated dissolution in alcohol and precipitation with water. Since the product still gave some colour with ferric chloride in alcoholic solution, it was again

subjected to methylation in the above manner and purified. The dried solid was finally dissolved in acetone and fractionally precipitated with petroleum ether. Some coloured impurities were precipitated first and were removed. Subsequently the methyl ether was obtained as an almost colourless amorphous solid. It now gave no colour with ferric chloride in alcoholic solution and did not dissolve in aqueous alkali.

Acetylation.—The purified kino (5 g.) was treated with acetic anhydride (15 g.) and anhydrous sodium acetate (5 g.) and the mixture refluxed on an oil-bath for 5 hours. After cooling, the mixture was poured into ice-water and the acetyl-kino that separated out, was filtered, washed with water and dried. It was then purified by crystallisation from chloroform-alcohol mixture whereby it was obtained as a colourless crystalline powder. To ensure complete acetylation, the acetylated product was boiled again with acetic anhydride and anhydrous sodium acetate for 5 hours. The contents were cooled and poured into ice-cold water. The solid that separated out was crystallised from chloroform-alcohol mixture. The final product was colourless and crystalline, but the shape was not definite when seen under the microscope (yield: 3·0 g.).

Butea gum.—The purification of Butea gum and the preparation of methyl and acetyl derivatives of the phlobatannin present in it were carried out exactly in the same manner as given in connection with gum kino. The appearance of the products was just the same.

Comparison of the phlobatannins.—The purified phlobatannins from the two sources gave identical colour and precipitation reactions with the following reagents: ferric chloride (aqueous and alcoholic), dark green precipitate; gelatin, flesh coloured precipitate; lead acetate, flesh coloured precipitate soluble in 10% acetic acid; boiling aqueous hydrochloric acid, red precipitate; bromine water, immediate orange precipitate; calcium hydroxide, gelatinous pink precipitate; nitrous acid, immediate brown precipitate; formaldehyde and dilute sulphuric acid with warming, flesh coloured precipitate.

Table I gives a comparison of the analytical data relating to the methyl ethers and acetates. The results obtained by Simonsen are also given in the table for purposes of comparison.

TABLE I

Compound	From Butea gum	From Malabar kino	Values for Malabar kino reported by Simonsen
Methyl ether—			
C %	60·5	60·5	61·7, 62·3
H %	5·5	5·9	5·5, 5·8
Methoxyl %	29·3	28·9	26·7, 26·9
$[\alpha]_D^{30°}$	204·5°	196·2°	
Acetate—			
C %	58·7	58·9	58·3, 58·2
H %	4·4	4·5	4·9, 4·8
$[\alpha]_D^{30°}$	174·9°	168·9°	

SUMMARY

The phlobatannin components of kino gum and Butea gum have been purified and rendered free from water and ether-soluble impurities. By subsequent methylation and acetylation almost colourless methyl ethers and acetates have been obtained. They exhibit marked optical activity thus supporting the idea that the phlobatannins are probably hydroxy-flavan derivatives. A comparison of the properties of the phlobatannins from the two sources and of their derivatives indicates that they are identical.

REFERENCES

1. Simonsen   .. *J. C S*, 1911, **99**, 1530.
2. Russel   . *Chem. Rev*, 1935, **17**, 165.
3. Biggs, Cooper, Hazleton,   *J. A C S*, 1931, **53**, 1504
   Nierenstein and Price

CHEMICAL COMPOSITION OF *CALOTROPIS GIGANTEA*

Part IV. The Resinols of the Root Bark

BY K. J. BALAKRISHNA, P. BHASKARA RAMA MURTI AND T. R. SESHADRI

(From the Department of Chemistry, Andhra University)

IN Part III[1] was described the study of the wax and resin components of the root bark of *Calotropis gigantea*. Besides β-amyrin, a resinol, mudarol was reported to be present in the form of ester with fatty acids of large and small chain lengths. It agreed with the general description given by the previous workers, Hill and Sirkar[2] in melting point, crystalline appearance and composition. Its properties were, however, definitely those of a resinol. It has now been shown to be a mixture consisting of two isomeric resinols, giganteol and isogiganteol. On acetylation with boiling acetic anhydride in the presence of sodium acetate, mudarol yields a product which after one crystallisation from alcohol-ether mixture melts at 195–96° agreeing with the melting point of mudarol acetate recorded by Hill and Sirkar. But, by repeated fractionation using ethyl acetate it could be separated into two fractions, (A) and (B). Fraction (A) melting at 252–53° is less soluble and is found to be identical with giganteol acetate[3] yielding giganteol on hydrolysis. Fraction (B) melts at 196–97° and yields a new alcohol melting at 177–78°. Several methods of acetylation have been examined. Milder conditions such as heating with acetic anhydride at 100° in the presence of anhydrous pyridine or treatment with acetyl chloride in the cold in the presence of anhydrous pyridine are found to be better.

That the above observations are not due to any structural change brought about by the acetylating agents has been proved in an independent way. The separation of the free alcohols, giganteol and isogiganteol from the mudarol mixture can be effected by chromatographic analysis using activated alumina and benzene-ligroin mixture. When the alcohols thus isolated are acetylated, they readily give the pure samples of giganteol and isogiganteol acetates. Mudarol seems to be an equimolecular mixture of the two alcohols.

The properties of the new alcohol, isogiganteol and of its acetate are recorded. From the composition of giganteol and isogiganteol it appears

138

possible that they are dihydric alcohols. But they form only monoacetates and no definite evidence for the existence of the second alcohol group has so far been obtained. The compounds do not react with 2 : 4-dinitrophenyl-hydrazine indicating the possible absence of carbonyl groups.

EXPERIMENTAL

Acetylation of mudarol.

(1) *With boiling acetic anhydride.*—Mudarol (3·5 g.) was dissolved in acetic anhydride (30 c.c.), sodium acetate (5 g.) added and the mixture boiled for 3½ hours. It was then cooled, treated with ice-water, allowed to stand for 10 hours and the resulting solid was filtered. When the product was crystallised from alcohol-ether mixture, it melted at 195–96°. This substance was then repeatedly crystallised from ethyl acetate when it was obtained in two fractions The top fraction melted at 252–53° and was identical with giganteol acetate On hydrolysis it gave rise to giganteol melting at 223–24°. The second fraction melted at 196–97°. There was great difficulty in effecting the separation of the mixture obtained by this method of acetylation Due to the smallness of the yields complete characterisation of the products was not attempted in this experiment.

(2) *With acetic anhydride and pyridine at* 100°.—Mudarol (2·0 g.) was dissolved in anhydrous pyridine (10 c.c.) and acetic anhydride (5 c.c.) was added. The contents were heated at 100° for 3½ hours. The mixture was then cooled and poured into a large volume of water when a colourless solid separated out. This crude product, on repeated crystallisation from ethyl acetate, could be separated into two sharp-melting crystalline products. The top fraction (I) melted at 252–53° and the fraction (II) from the mother-liquors melted at 196–97°.

Fraction I (Giganteol acetate).—This was a colourless solid and appeared as elongated hexagonal plates under the microscope. It dissolved in benzene, chloroform and ether but was insoluble in alcohol. When mixed with an authentic sample of giganteol acetate, the melting point was not depressed (252–53°). $[\alpha]_D^{28°}$, $+98\cdot5°$ in benzene solution. (Found: C, 79·1; H, 11·1; $C_{32}H_{52}O_3$ requires C, 79·3; H, 10·7%.)

Giganteol.—The above solid (0·2 g.) was hydrolysed by boiling with 7% alcoholic potash. When the reaction mixture was concentrated and allowed to cool slowly, crystals of the free alcohol separated out. After one crystallisation from alcohol it melted at 223–24° and appeared as rectangular rods under the microscope. There was no change either in melting point or crystal structure on further crystallisation. It did not form a hydrazone

A2

with 2-4-dinitrophenyl-hydrazine. $[\alpha]_D^{28°}$, $+111.2°$ in benzene. The colour
reactions were the same as those of giganteol. The mixed melting point with
an authentic sample of giganteol was undepressed.

Fraction II (Isogiganteol acetate).—This was a colourless solid and
appeared as tiny plates under the microscope. It was soluble in ether,
chloroform and benzene in the cold and in boiling alcohol. It gave a pink
colour with the Liebermann-Burchard reagent and a yellow solution exhi-
biting green fluorescence with the Salkowski reagent. (Found: C, 79·8;
H, 10·8; $C_{42}H_{56}O_3$ requires C, 79·3; H, 10·7%.) The mixed melting
point of this compound with giganteol acetate was found to be depressed
(175–80°). $[\alpha]_D^{40°}$, $+96.2°$ in benzene solution.

Isogiganteol.—The above compound (0·2 g.) was hydrolysed by boiling
with 7% alcoholic potash. When the reaction mixture was concentrated,
a colourless solid separated out. It was crystallised from alcohol, when a
glistening crystalline solid (hexagonal plates) melting at 177–78° was obtained.
With the Liebermann-Burchard and Salkowski reagents it gave the same
colour reactions as giganteol and the calotropeols. There was no change
either in melting point or crystal structure on further crystallisation. It
did not react with 2-4-dinitrophenyl-hydrazine. $[\alpha]_D^{28°}$, $+97.4°$ in benzene
solution. (Found: C, 82·0; H, 11·1; $C_{40}H_{66}O_2$ requires C, 81·4; H,
11·3%.)

(3) *With acetyl chloride and pyridine at 0°* — Mudarol (0·5 g.) was
dissolved in anhydrous pyridine (10 c.c.) and the solution was cooled to 0°.
Acetyl chloride (2 c.c.) was added drop by drop, all the while taking care to
see that the contents were stirred well and that the temperature was maintained
at 0°. After the addition of all the acetyl chloride the mixture was heated
on a boiling water-bath for 2 minutes and poured into a large volume of
water. The crude reaction product which separated out, was repeatedly
crystallised from ethyl acetate when two fractions, one melting at 252–53°
and the other melting at 196–97° were obtained just as in the previous
acetylation and the products were the same. The yields in methods 2 and 3
were equally good and the separation was not very difficult. The two
resinols appeared to be present approximately in equal amounts.

Chromatographic analysis of mudarol.

Mudarol (3·5 g.) was dissolved in 150 c.c. of benzene-ligroin (b.p. 60–80°)
mixture (5 : 3) and the solution allowed to pass down a column (20 cm. by
2½ cm.) of activated alumina (B.D.H.) under gentle suction. The column
was then successively washed with the same solvent using 100 c.c. each time.

Each fraction was collected separately and the dissolved solid, by crystallisation from the same solvent, obtained in two crops, the final mother liquor being discarded. Details of the analysis are given below:

Serial No.	Fraction	Yield in grams	I Crop Melting point	I Crop Crystal structure	II Crop Melting point
1	Original filtrate	Nil			
2	Benzene-ligroin (5 . 3)	Nil			
3	do	Nil			
4	do	0·2	176–77°	Long and soft needles	176–71'
5	Benzene-ligroin (6 . 2)	0 65	176–77°	do	177–78°
6	do	0 52	177–78°	Hexagonal plates	176–77°
7	do	0·68	177–78°	Elongated plates and flat needles	179–80°
8	Benzene-ligroin (6 1)	0 41	185–86°	do	196–98°
9	do	0·30	189–90°	Broad plates and needles	200–01°
10	do	0·33	193–94°	do	200–01°
11	Benzene	0 21	197–98°	do	209–10°
12	do.	0 06	203–04°	do	209–10°
		3·36			

Crop I of fractions 4, 5 and 7 and crop II of fractions 4, 5, 6 and 7 (*i.e.*, fractions melting below 180°) were put together as 'A'. Crop I of fraction 6 had a remarkably uniform crystal structure and seemed to be quite pure. Hence it was kept separately. Its mixed melting point with isogiganteol was undepressed. On acetylation using acetic anhydride and pyridine it gave a pure sample of isogiganteol acetate melting at 196–97° after one crystallisation from ethyl acetate. Crop I of fractions 8, 9 and 10 (*i.e.*, those melting between 185–93°) was put together and marked ' B '. Crop I of fractions 11 and 12 and crop II of fractions 8, 9, 10, 11 and 12 (*i.e.*, those melting above 197°) were put together as ' C '

Analysis of 'A'—The substance was dissolved in 50 c.c. of benzene-ligroin mixture (5 : 3) and was passed down a column of activated alumina (10 cm. by ½ cm.). Fractional elution was done using 25 c.c. of the same solvent in each case.

Serial No	Fraction	Melting point	Crystal structure	Yield in grams
1	Original filtrate			Nil
2	Benzene-ligroin (5 . 3)	180–82°	Needles	0·10
3	do	170–73°	Plates and needles	0·15
4	do	177–78°	Hexagonal plates	0·10
5	do	177–78°	do.	0·10

The last two fractions were mixed together and the substance was found to be identical with crop I of fraction 6 and with isogiganteol in melting point and crystal structure. On acetylation with acetic anhydride and pyridine and after one crystallisation of the reaction product from ethyl acetate, a pure sample of isogiganteol acetate melting at 196–97° was obtained.

Substance ' B '.—On acetylation using the same method as above, a crystalline solid melting at 252–53° was obtained after one crystallisation from ethyl acetate and it was identical with giganteol acetate in melting point and crystal structure. This fraction seemed to contain giganteol as the major component.

Analysis of ' C '.—The substance was dissolved in 50 c.c. of benzene-ligroin (5 : 3) mixture and passed down a column of activated alumina (10 cm. by ½ cm.) Fractional elution was done using 25 c.c. of the solvent each time.

Serial No	Fraction	Melting point	Yield in grams
1	Original filtrate		Nil
2	Benzene-ligroin (5 · 3)	193–95°	0·05
3	do	185–87°	0·10
4	do	178–81°	0·10
5	do	195–97°	0·08
6	do	220° (sintering at 216°)	0 10

The last fraction when crystallised from benzene melted sharp at 223–24° and appeared as rectangular rods under the microscope. A mixed melting point of this substance with giganteol was found to be undepressed Acetylation of the substance using acetic anhydride and pryidine gave a product which on crystallisation from ethyl acetate melted at 252–53°. It was identical with giganteol acetate in melting point and crystal structure.

SUMMARY

Mudarol, the chief resinol component of the root bark of *Calotropis gigantea*, has been separated into two isomeric compounds by fractional crystallisation of the acetates and also by chromatographic adsorption analysis of the free alcohols. Giganteol which was first obtained from the stem bark is one of them and a new triterpene alcohol, isogiganteol is the other. The properties and reactions of the new resinol are described. Though giganteol and isogiganteol ($C_{30}H_{50}O_4$) have two oxygen atoms they form only monoacetates. They do not combine with dinitrophenyl-hydrazine.

REFERENCES

1. Murti and Seshadri . Proc. Ind. Acad. Sci., A, 1945, **21**, 147.
2. Hill and Sirkar .. J. C S, 1915, 1437
3. Murti and Seshadri . Proc. Ind. Acad. Sci., A, 1945, **21**, 17.

CHEMICAL COMPOSITION OF *CALOTROPIS GIGANTEA*

Part V. Further Examination of the Latex and Root Bark

By K. J. Balakrishna, S. Rajagopalan and T. R. Seshadri

(From the Department of Chemistry, Andhra University)

Received August 22, 1945

In Part I of this series[1] a detailed examination of the wax and resin compo-
nents of the latex of *Calotropis gigantca* was reported. The coagulum
obtained by the addition of alcohol to the latex could be separated into
two major fractions The fraction soluble in ether and alcohol consisted
of a resinol mixture from which two new resinols, α- and β-calotropeols and
β-amyrin could be isolated and characterised The alcohol and ether-
insoluble portion of the coagulum was not examined in detail The aqueous
alcoholic filtrate from the coagulum, when extracted with chloroform,
yielded a fraction whose properties and reactions indicated that it contained
cardiac poisons. This too was not examined further. From the aqueous
alcoholic mother-liquor left over, calcium oxalate was slowly deposited on
long standing.

   An attempt has now been made to complete the examination of the
latex reported in Part I. The non-resinol portion of the coagulum has been
found to consist mainly of caoutchouc. A quantitative estimation shows
that caoutchouc forms 1·3% of the latex. A small amount of inorganic
matter consisting mainly of calcium, oxalate, sulphide and phosphate is
also present in the coagulum. The proportion of this is greater if larger
volumes of alcohol are used for the coagulation of the latex or if the
coagulum and the aqueous alcoholic portion are allowed to stand together
for longer periods before filtration. The inorganic matter gets slowly
precipitated after the addition of alcohol.

   In the estimation of caoutchouc referred to above, acetone is employed
for the removal of the more soluble components from the coagulum. This
solvent is found to be more efficient than ether and alcohol for separating
the resinols completely from the accompanying caoutchouc and' mineral
matter. When examined by the acetylation and benzoylation methods as
already described just the same components are obtained from this resinol
fraction in a better yield. During the course of this work a number of

143

samples of the resinol mixture have been examined in detail. It seems to be definite that α- and β-calotropeols exist in the latex as such and are not produced by the reagents used for the separation. Even after a single crystallisation of the crude resinol mixture from rectified spirit a product is obtained which analyses essentially for the formula $C_{30}H_{50}O$ though small quantities of substances with the formula $C_{30}H_{50}O_2$ are rot excluded. In another communication[2] it has been shown that resinols with the latter formula which occur in the plant are also stable to the action of ordinary reagents. Further it has now been found that by repeated fractional crystallisation of the resinol mixture from the latex it is possible to obtain a small amount of α-calotropeol which is definitely pure.

For the isolation of cardiac poison from the aqueous alcoholic filtrate, observance of certain precautions has been found to be quite necessary for ensuring purity and yield. The substance is unstable to heat particularly in the presence of air and water and heating has to be avoided as far as possible. The resulting product has been carefully examined for the presence of more than one component, as in the work on the heart poisons of *Calotropis procera* by Hesse[2]; but only one entity is found to be present. The properties of this substance which contains nitrogen and sulphur and is poisonous to fish, resemble those of uscharin (isolated by Hesse) qualitatively but the two exhibit marked differences in details. It appears to be new and is therefore tentatively given the name ' gigantin '.

Properties	Uscharin	Gigantin
1. Crystal form ..	Fine needles	Small rectangular plates
2 Decomposition point ..	265°	243°
3 Optical Rotation $[\alpha]_D^{10}$ ..	29 0°	29·8°
4. Elements	C, 63·4; H, 7·0; N, 2·4 and S, 5·5%	C, 56·2; H, 7·1, N, 1·4 and S, 4·2%
5. Legal test .	Positive	Positive
6. Hydrolysis with sulphuric acid	Uscharidin	Decomposition products

An examination of the root and stem barks of *Calotropis gigantea* has also been carried out with a view to see if they contain compounds of the cardiac poison group. The dry material is deprived of its wax components by extraction with petroleum ether and is then extracted with chloroform to get the cardiac poison. Here again it has been found that if continuous extraction using boiling solvent is employed the cardiac poison is destroyed as a result of the prolonged heating of the extract in the receiver, while if cold percolation is used and the solvent removed by distillation *in vacuo*

the residue gives definite tests for the presence of heart poisons. The stem bark is a very poor source; the root bark is much better though the product is very difficult to purify. Undoubtedly the latex is the best source.

There are two varieties of *Calotropis gigantea* which differ in the colour of the flowers. The purple coloured variety is more common and the white one is somewhat rare. The latter is considered to be more medicinal and more toxic than the former. In the course of the present studies the root bark of the white flowered variety has been found to contain much higher proportion (1½ to 2 times) of resinols and also of the cardiac poison.

<div align="center">EXPERIMENTAL</div>

Estimation of caoutchouc.—A weighed amount of the dry coagulum (15 g.) was extracted thrice with boiling acetone (50 c.c each time). This removed all the resinol portion. The residue was then boiled with a considerable excess of carbon tetrachloride or chloroform (150 c.c.). When no more solid went into solution, the supernatant solution was carefully filtered off from the small amount of inorganic residue. After washing the filter with a little more solvent the combined filtrate was distilled to recover most of the solvent. The residue was heated on a water-bath to remove the remaining solvent, dried in a steam oven, cooled and weighed (yield, 1·3% calculated on the latex). This substance, when dissolved in carbon tetrachloride gave a solution which was quite viscous and resembled commercial rubber solutions. The residue obtained after the removal of the solvent was flexible and elastic, and could be vulcanised by the usual methods employing sulphur and an accelerator.

Resinols in the coagulum.—The hot acetone extract was allowed to cool when a colourless solid was obtained. After the solvent was removed by distillation, a further quantity of the solid, which was slightly coloured, was obtained. Both the fractions gave colour reactions characteristic of resinols. So they were combined and saponified in benzene solution by boiling with 7% alcoholic potash. After removal of the solvents and addition of water to the concentrate, the unsaponifiable matter was extracted with ether, the ether solution dried over calcium chloride, and the solvent removed by distillation. A portion of the residue was crystallised from rectified spirit. A colourless solid was obtained in the form of flakes and it gave the following values when analysed for carbon and hydrogen: (Found: C, 83·8; H, 11·4; $C_{30}H_{50}O$ requires C, 84·5; H, 11·7% and $C_{60}H_{50}O_2$ requires C, 81·4; H, 11·3%.)

The bulk of the unsaponifiable portion (m.p. 110–50°) of the coagulum (33 g.) was crystallised from benzene-alcohol (1 : 3) mixture fifteen times

when the melting point went up to 205-10°. Four further crystallisations from alcohol effected further rise in the melting point to 220-21° and this did not change on further crystallisation. The product (0·2 g.) was quite crystalline (transparent rods and narrow rectangular plates) and was identical with α-calotropeol obtained by the acetylation method in melting point and crystal structure. This sample was acetylated using acetic anhydride and sodium acetate when an acetate melting at 251-52° was obtained and this was identical with α-calotropeol acetate. Saponification of the acetate by boiling with 7% alcoholic potash yielded the original resinol again. On treatment with excess of bromine α-calotropeol acetate formed a bromo-derivative melting at 211-12°.

Isolation of gigantin.—The fresh latex was treated with an equal volume of alcohol and the mixture vigorously stirred. The coagulum that separated from the aqueous alcoholic solution was filtered after standing for an hour. The filtrate was concentrated *in vacuo* to remove alcohol as far as possible and the aqueous residue was repeatedly extracted with chloroform. The combined chloroform extract was washed with a little water, dried over calcium chloride and then evaporated under reduced pressure employing a very small stream of carbon dioxide to ensure smooth boiling. The residue was taken up in a small volume of chloroform and diluted with petroleum ether, added in small quantities at a time, the mixture being shaken after each addition. The clear solution was decanted off from the sticky residue which was obtained at each addition before adding the next portion of petroleum ether. When the precipitate obtained was no longer sticky but granular it was diluted with a large excess of petroleum ether and the solid filtered. Crude gigantin was thus obtained in a yield of 1% of the weight of the latex.

The purification was effected by dissolving the solid again in the minimum amount of chloroform and adding petroleum ether. After several repetitions of this process pure gigantin was obtained as small rectangular plates decomposing at about 243°. It gave the following values on analysis: C, 56·2; H, 7·1; N, 1·4; S, 4·2%. It had a specific rotation of + 29 6° at 30°, in chloroform. Though nitrogen was one of the component elements it could not be detected qualitatively by Lassaigne's test evidently because of its low percentage but the presence of sulphur was easily indicated. Further an alcoholic solution gave a red colour with alkaline sodium nitroprusside (positive legal test). It dissolved in concentrated hydrochloric acid producing a greenish blue solution. With the Liebermann-Burchard reagent a green solution was obtained and the colour of the solution changed

to red after a day. The substance tasted bitter and left a tingling sensation on the tongue and it was toxic to fresh-water fish. When an attempt was made to hydrolyse it with N/2 methyl alcoholic sulphuric acid only an intractable product was obtained. Under similar conditions uscharin has been reported to give rise to uscharidin (Hesse, *loc. cit.*).

EXAMINATION OF THE ROOT BARK FOR CARDIAC POISONS

The dried bark was exhausted with petroleum ether in a continuous extractor to remove wax and the remaining material air-dried. It was subsequently percolated with cold chloroform and the percolate evaporated under reduced pressure using a small stream of carbon dioxide. The residue was treated further just as in the experiment with the aqueous alcoholic filtrate of the latex; it was very difficult to purify. The final product, obtained in very poor yield, was crystalline-looking and colourless and decomposed at about 210° Due to dearth of material further purification could not be effected. The product, however, was toxic and gave all reactions of gigantin (yield, 0 1 g. from 1·5 kg of the dry root bark)

SUMMARY

The latex of *Calotropis gigantea* contains caoutchouc to a small extent, 1·3%. The resinols are best separated from the coagulum by means of acetone. The mixture consists essentially of resinols having the formula $C_{30}H_{50}O$ and by repeated fractional crystallisation a very small yield of α-calotropeol could be obtained. The toxic principle of the latex, gigantin, contains nitrogen and sulphur and resembles uscharin in several respects, but differs from it in composition and in its behaviour on hydrolysis.

REFERENCES

1. Murti and Seshadri   . *Proc Ind Acad Sci*, A, 1943, **18**, 145.
2. Hesse *et al*   *Ann*, 1939, **537**, 67.
3. Balakrishna, Murti and . *Proc Ind Acad Sci*, A, 1945, **22**, 138.
   Seshadri

PIEZO-ELECTRIC AND ELECTRO-OPTICAL KERR EFFECTS IN CRYSTALS : APPLICATION OF GROUP THEORY

By D. SURYANARAYANA

(From the Department of Physics, Andhra University, Guntur)

1. INTRODUCTION

BHAGAVANTAM (1942) described a simple method of obtaining the number of independent constants necessary to describe the elastic and photo-elastic behaviour of the 32 crystal classes and reported some remarkable results for photo-elasticity in the case of certain classes. While the number of elastic constants obtained by this method agree in all cases with the well-known results, the numbers of stress-optical constants are at variance with those given by Pockels in some cases. The results obtained by him had been confirmed by a direct calculation of the non-vanishing constants for all the 32 classes In the present paper the above method is applied to obtain the number of independent piezo-electric and electro-optical Kerr constants for the 32 classes The numbers obtained agree with those derived by direct methods in all cases.

2. THE METHOD

The piezo-electric constants and moduli connect the three components of the electric moment vector and the components of the second order strain and stress tensors respectively. The electro-optical Kerr constants connect the components of the electric field vector and the optical coefficients. Hence in both cases, the constants, which are 18 in number in a general case, transform as products of the vector and the tensor components. For an operation R_ϕ consisting of a rotation through ϕ or a rotation reflection through ϕ the co-ordinates transform as below ·

$$x \to x \cos \phi + y \sin \phi; \ y \to - x \sin \phi + y \cos \phi; \ z \to \pm z.$$

The plus and minus sign where the alternative occurs refer to cases of simple rotation and rotation reflection through ϕ in the order in which they are given From the transformation matrix for the constants, it can easily be shown that the character appropriate to R_ϕ is $2 \cos \phi \pm 8 \cos^2 \phi + 8 \cos^3 \phi$. Then the number of coefficients n appropriate to any crystal class is given by the formula*

$$n = 1/N \ \Sigma h_i \chi_i' \ (R),$$

---

* For further details, reference may be made to the above paper by Bhagavantam

where N is the total number of elements in the corresponding point group, h_j the number of elements in the jth conjugate class of the point group and $\chi_j{}'(R) = 2\cos\phi \pm 8\cos^2\phi + 8\cos^3\phi$.

3. RESULTS

Applying the above formula to the 32 classes, it can easily be seen that the number n for the 11 classes which possess a centre of symmetry vanishes. This is a well-known result. The numbers in the remaining classes are given in Table I. It may be noted that all the constants vanish for the class O, although there is no centre of symmetry.

TABLE I

Symbol	Symmetry operations	n
C_1	E	18
C_s	E σ_h	10
C_2	E C_2	8
C_{2v}	E C_2 σ_v σ_v'	5
D_2	E C_2 C_2' C_2''	3
C_4	E $2C_4$ C_2	4
S_4	E $2S_4$ C_2	4
C_{4v}	E $2C_4$ C_2 $2\sigma_v 2\sigma_v'$	3
D_{2d}	E C_2 C_2' C_2' σ_D $2'_4$ σ_v'	2
D_4	E $2C_4$ C_2 $2C_2$ $2C_2'$	1
C_3	E $2C_3$	6
C_{3v}	E $2C_3$ $3\sigma_v$	4
D_3	E $2C_3$ $3C_2$	2
C_{3h}	E $2C_3$ σ_h $2S_3$	2
C_6	E $2C_6$ $2C_3$ C_2	4
D_{3h}	E $2C_3$ $3C_2$ σ_h $2S_3$ $3\sigma_v$	1
C_{6v}	E $2C_6$ $2C_3$ C_2 $3\sigma_D$ $3\sigma_v$	1
D_6	E $2C_6$ $2C_3$ C_2 $3C_2$ $3C_2'$	1
T	E $3C_2$ $8C_3$	1
T_d	E $8C_3$ $3C_2$ 6σ $6S_4$	1
O	E $8C_3$ $3C_2$ $6C_2$ $6C_4$	0

4. SUMMARY

The method given by Bhagavantam has been extended for the purpose of obtaining the number of independent constants needed to describe the piezo-electric and the electro-optical Kerr effects in the 32 classes of crystals. The results agree in all cases with those derived directly.

The author wishes to express his grateful thanks to Prof. S. Bhagavantam for his kind encouragement.

REFERENCE

S Bhagavantam   *Proc Ind Acad. Sci.*, A, 1942, **16**, 359.

RAMAN SPECTRA OF MIXED CRYSTALS

Sodium and Potassium Nitrates

By M Kanaka Raju

(From the Department of Physics, Andhra University Guntur)

Received July 31, 1945

(Communicated by Prof. S Bhagavantam, F A Sc)

1. Introduction

Gerlach[1] investigated the Raman effect in a eutectic mixture of sodium nitrate and potassium nitrate and observed a sharp Raman line, when the mixture was freshly prepared. The frequency shift is midway between the frequencies characteristic of the NO_3 ion in the two crystalline nitrates. The Raman spectrum of the same eutectic, when investigated after about 96 hours, revealed the presence of two Raman lines characteristic of pure. $NaNO_3$ and pure KNO_3. However, sodium and potassium nitrates do form a continuous series of mixed crystals only above 130° C., when the two lattices of the individual crystalline salts unite to form a unique lattice. So long as the temperature is above 130° C., whatever be the time for which the eutectic is kept, its Raman spectrum should give a single line character-istic of the unique lattice of the mixed crsytal.

In the present investigation, the author has undertaken an exhaustive study of the mixed crystals of Na and K nitrates of different compositions and at different temperatures.

2. Experimental Technique

The purification of the substances is effected by repeated crystallisations from aqueous solutions, using chemically pure water Scrupulous care was taken to see that all the dry glass vessels used were free from dust particles. Saturated solutions of the crude salts in distilled water, made at temperatures slightly above room temperature, were filtered through a double filter-paper into the clean and dry evaporating dishes, kept in glass cases. Beakers of concentrated sulphuric acid are also kept by the side of the crystallising dishes to hasten crystallisation. Each crystallisation has taken nearly a week or two, depending on the saturation of the solution taken. Pure transparent crystals are picked up by means of a clean forceps and these are crystallised

again. Thus six successive recrystallisations were effected in each case and the products are used in the investigations.

Throughout the investigations, arrangements had to be made to keep the mixture above 130° C. Specially constructed electric furnaces are used to raise the temperature of the Raman tube and keep it at the desired point. The container is a pyrex glass tube of diameter about ¼" with a window set at one end for the observation of scattered light and bent at right angles at the other end into the form of a bulb of diameter 1½" and a long neck. The purified substances are dried in a steam oven for two or three hours, cooled, powdered and weighed quantities of sodium and potassium nitrates in the required proportion are packed into the Raman tube and the bulb, whose diameter is so chosen to suit the condition of the experiment.

Usual illumination arrangements employing an 8″ glass condenser have been used. The Raman tube is jammed against an aperture in an asbestos screen, held in position. A Hilger 2-prism glass spectrograph of high light-gathering power is used in the investigations. In the case of the melts, the 1050 cm.$^{-1}$ line could be clearly seen visually through the spectrograph and an exposure of 4 to 5 hours on Ilford Selochrome plates was found sufficient even with a small Raman tube to give pictures of such intensity that the overtone line is well recorded. For the mixed crystals, the melt in the Raman tube is very slowly and steadily cooled to give a reasonably transparent crystal. Very narrow and small tubes are chosen, as even a small transparent bit is sufficient to give a good Raman spectrum. It may be remarked then that during an exposure, the supply of electric current should be continuous. Any interruption resulting in the tube going below 130° C. meant potassium nitrate changing from rhombohedral to the orthorhombic variety and the tube invariably cracked.

3. RESULTS

The results obtained are given in Tables I, II and III :—

TABLE I

Melts of NaNO$_3$ and KNO$_3$

% Proportion of NaNO$_3$	% Proportion of KNO$_4$	Temp. °C.	Frequencies in cm^{-1}			
100	0	330	715	1054	1322-1468	1661
75	25	320	718	1052	1322-1400	1658
45	55	300	717	1051	1320-1455	1660
25	75	320	717	1049	1316-1456	1655
0	100	350	718	1046	1313-1448	1656

TABLE II

Mixed Crystals at 190° C.

% of NaNO₃	% of KNO₃	Frequencies in cm⁻¹
75	25	1064
45	55	98, 158, 718, 1059, 1372
25	75	1052

TABLE III

45% NaNO₃ and 55% KNO₃

Nature of state	Principal frequency
Mixed Crystal at 190° C	*Single* line at 1059
Mixture at 30° C.,	*Double* lines at 1048, 1068

4. DISCUSSION OF RESULTS

The experimental data regarding the Raman spectra of inorganic nitrates show that the vibrational frequencies characteristic of the NO₃ ion are not the same under different conditions. When the same ion is associated with different cations in the crystalline state, it exhibits slightly different frequencies. The arguments of I. R. Rao,⁵ that the nitrogen atom in the different nitrates is displaced to different degrees from the plane containing the oxygen atoms, are far from justified. The available X-ray data do not confirm Thatte and Ganesan's suggestion that the distance between the nitrogen atom and the surrounding oxygen atoms is different in different nitrates. Sankaranarayana¹ has recently given a satisfactory explanation for the above experimental results. According to this author, the increase in the frequency shifts of the internal vibrations of the ion is caused by the potential field around it, which arises due to the rest of the crystalline structure. The distribution of the field strength determines the particular orientation which the ion assumes in the crystal. In the lattice oscillations, the ions as a whole move in the potential field and the primary forces that come into operation are mainly those due to the field, the forces operating in the ion itself being negligible. During the internal oscillations of the ion, in addition to valence forces between constituent atoms, subsidiary forces due to potential field have to be taken into account. It is these forces that stand against the freedom of movement of the constituent particles of the ion and cause the frequency to be enhanced. Thus the changes in frequency

in the solution and the crystal can be explained, by correlating the changes in vibrational frequencies with the lattice frequencies of the crystal.

We have now to consider why there is a change in frequency as we move from one crystalline nitrate to another, the anion being the same and the cation changing. It is observed that, for the cations having the same valency, the frequency decreases with increasing volume. A possible explanation may be furnished by considering the fact that every cation will be surrounded by a certain number of negative ions, to keep the structure as a whole electrically neutral. That is to say, with increasing volume, the number around each negative ion diminishes. It has been already stated, that the potential field around the ion is primarily contributed by these oppositely charged neighbours round it and hence with increasing volume, the field strength diminishes or the frequency shift tends more and more to the normal value of the ion in the solution. From the above explanation, it can be understood why there is a shift of 20 cm.$^{-1}$ in the principal frequency of the NO_3 ion as between $NaNO_3$ and KNO_3, in the crystalline state Above 130° C., potassium nitrate changes to rhombohedral form. At such temperatures sodium and potassium are thus associated with the same NO_3 ion in the same crystal structure, but the frequency in potassium nitrate is definitely lower than that in sodium nitrate by about 18 wave numbers. This is apparently due to the change in radii of the cations that of sodium being 0·98 A.U. and of potassium being 1·33 A.U. In the fused state, on the other hand, the frequency can be seen to be intermediate between the one found in solution and that found in the crystal.

The frequency shift of the total symmetric oscillation of NO_3 ion in $NaNO_3$ melt is 1054, while that in KNO_3 melt is 1046 and from the results obtained by the author at intermediate concentrations, it can be readily seen that there is a gradual variation of frequency from the value of 1054 of $NaNO_3$ to 1046 of KNO_3 as more and more of potassium nitrate is added. For the doubly degenerate vibration at about 1400 also, a gradual variation in frequency can be observed. It is obvious that the fused state is intermediate between that of the solution and of the crystal. The variation in frequency in the fused state may be attributed to the local fields in the dense fluid.

From Table III, it is seen that in the mixed crystal the total symmetric oscillation is represented by a single line. At the room temperature, the Raman spectrum taken by the author, of a mixture of sodium and potassium nitrates in the same critical composition using iodine in carbon tetrachloride as filter to eliminate the continuous spectrum, revealed the presence of 2

lines at frequency shifts 1048 and 1068. These represent the total symmetric vibrations in sodium and potassium nitrates respectively. There is a lowering of not more than 3 wave numbers in the frequency shifts of both sodium and potassium nitrates even at high temperatures, as can be seen from Nedungadi's results, and the difference of nearly 20 wave numbers, between the two crystals is still maintained. The frequency shift in the mixed crystal of composition at 190° C. is intermediate to those of sodium and potassium nitrates at this temperature. The intermediate value to be expected, in a mixed crystal of critical composition, will be 1058 cm.⁻¹, if sodium in sodium nitrate is replaced by potassium in direct proportion to the two constituents present. This is in excellent agreement with the observed value of the author at 1059.

The presence of a single line in the mixed crystal of critical composition and the presence of two lines in a mixture of the same composition clearly confirm that in the mixed crystal the two lattices of the sodium and potassium nitrates unite to form a unique lattice From the observations, it can be concluded, that the frequency is in direct proportion to the constituents present in the mixed crystal and a gradual variation should be expected as concentration is changed.

A diffuse line at 1372 and another at 718 cm.⁻¹ have been recorded in the mixed crystal of the critical composition. Thus the three fundamental frequencies characteristic of the NO_3 ion are recorded in the mixed crystal. The diffuse line in potassium nitrate has a value of about 1350 at high temperatures and that of sodium nitrate at 1380. The value obtained in the mixed crystal of critical composition is intermediate between the two and hence the same argument as in the case of the total symmetric vibration will also hold here.

Bhagavantam and Venkatarayudu[5] have worked out the modes of oscillation of sodium nitrate crystal. The unit cell of sodium nitrate contains two molecules and we should expect two lattice oscillations and three internal modes of oscillation to be active in Raman effect in this crystal. Accordingly the Raman spectrum of sodium nitrate consists of 5 lines at 98, 189, 727, 1070 and 1389. Sodium nitrate and potassium nitrate form mixed crystals only above 130° C. (*i.e.*) when potassium nitrate changes from orthorhombic to the rhombohedral form. Consequently the mixed crystal must be rhombohedral in form and its Raman spectrum should consist of two lattice oscillations again. The Raman lines observed in the case of the mixed crystal of critical composition at 718, 1059 and 1372 correspond to the internal modes of oscillation, and the broad lines at 98 and 158 correspond to the lattice oscillations.

Nedungadi's[6] results about the thermal effects in potassium nitrate do not clearly indicate the position of the lattice lines at a temperature of 190° C. The position of the lattice lines in the mixed crystal can be satisfactorily interpreted only if we know definitely the position of the lattice lines in potassium nitrate and sodium nitrate at the temperature of 190° C. In the absence of details, we can only conclude that the mixed crystal of sodium and potassium nitrates at the critical temperature of a temperature of 190° C. consists of a unique lattice, giving 2 lattice lines and 3 internal oscillations, in accordance with the theory.

Mixed crystals of compositions 75% $NaNO_3$ and 25% KNO_3, 25% $NaNO_3$ and 75% KNO_3 are also investigated. In each case, in spite of repeated trials, only the total symmetric vibration of the NO_3 ion is recorded. The tube, while hot, revealed small perfectly transparent crystals, in the form of microcrystals. When a fused mixture of the above composition is cooled, mixed crystals of somewhat varying composition will be obtained and it is impossible to grow a good single crystal, in a case other than the critical composition. This case is equivalent to obtaining the Raman spectrum of a substance in the form of crystalline powders.

It may now be concluded that in solution, the complex ions have independent existence and hence there is no variation of frequency with different cations. The fused state on the other hand appears to be intermediate between those of the solution and the crystal. In the mixed crystal, there is a gradual change of properties from sodium nitrate to potassium nitrate, as more and more potassium is added to replace sodium.

5. Summary

The experimental technique adopted by the author for obtaining clear and intense spectrograms in the case of melts as well as crystals of $NaNO_3$ and KNO_3 is described. A difference in frequency of nearly 20 wave numbers in the principal oscillation of sodium and potassium nitrates in the crystalline state is associated with difference in the volume of the two cations. The variation in frequency in the fused state, though not so marked as in the crystalline state, is attributed to the local fields in the dense fluid. In the case of the mixed crystal of critical composition, lines at frequency shifts 98, 158, 718, 1059 and 1372 are observed It is concluded that the mixed crystal forms a unique lattice. The frequency shifts 98 and 158 correspond to the lattice, while the other three are due to the internal oscillations. Mixed crystals of compositions 75% $NaNO_3$ and 25% KNO_3, and 25% $NaNO_3$ and 75% KNO_3 are also studied. A gradual variation of frequency from that of pure sodium nitrate to that of pure potassium

A3

nitrate, as concentration is changed in the mixed crystal is observed. **This** result and the fact that there is a unique line representing the total symmetric vibration in the mixed crystals (a mixture of the same composition revealing two lines characteristic of $NaNO_3$ and KNO_3 separately) confirm the formation of a unique lattice in the mixed crystal, the vicarious elements replacing one another, atom for atom.

In conclusion, it is a pleasure to express the author's grateful thanks to Prof. S. Bhagavantam under whose guidance and kind encouragement these investigations have been carried out.

REFERENCES

1. Gerlach . *Sitzungsb d math—naturw Abt*, 1932, **1**, 39.
2. Briscoe and Madgin *J Chem Soc*, 1923, **123**, 1608
3. Rao, I R *Proc Roy Soc*, 1934, **144**, 159
4. Sankaranarayana . *Thesis submitted to Andhra University*, 1943.
5. Bhagavantam and Venkata-rayudu *Proc Ind Acad Sci*, 1939, **9**, 224
6. Nedungadi *Ibid*, 1941, **14**, 242

8-HYDROXY-GALANGIN

By P. Ramachandra Rao and T. R. Seshadri

(From the Department of Chemistry, Andhra University)

AMONG the flavonols having the 5:7:8-orientation of hydroxyl groups, gossypetin was the first to be discovered and studied. It has been found in the Indian and Egyptian cotton flowers and in the flowers of *Hibiscus sabdariffa*. More recently herbacetin and hibiscetin have been isolated. The former is present in the flowers of *Gossypium herbaceum* and *Thespesia populnea* both free and as glucoside. Hibiscetin has so far been found to occur only in *Hibiscus sabdariffa*. The lowest member of the series, 8-hydroxy-galangin has not yet been isolated from natural products. It may however, be expected to occur and hence a study of this substance and of its derivatives is reported in this paper.

The synthesis of hydroxy-galangin has been effected on the same lines as the synthesis of gossypetin and herbacetin by Robinson and his co-workers,[1] but the required ketone, 2.4-dihydroxy-ω-3:6-trimethoxyacetophenone (II) is made by the simplified procedure of Rao, Rao and Seshadri[2] as described in connection with the synthesis of hibiscetin. It has been possible to isolate the 7-benzoyloxy derivative (III) as product of the Allan-Robinson condensation of the above ketone with benzoic anhydride and sodium benzoate. Subsequent hydrolysis yields 7-hydroxy-3:5·8-trimethoxy-flavone (IV). Demethylation of (IV) produces the tetrahydroxy flavone, 8-hydroxy-galangin (V) and methylation of (IV) forms the tetramethyl ether (VI). The tetramethyl ether has also been obtained directly by repeating the above condensation using 2-hydroxy-ω:3:4:6-tetramethoxy-acetophenone (VII), the so called gossypetol tetramethyl ether[7] since it was first obtained by the alkaline fission of hexamethyl gossypetin. We have now been able to carry out the fission of pentamethyl herbacetin[8] (VIII) using sufficient quantities and isolate this ketone in good yield. This reaction is an important support for the constitution of herbacetin and could not be done earlier due to lack of material. It may be mentioned here that herbacetin is best methylated by means of dimethyl sulphate and potassium carbonate in anhydrous acetone medium.

The new flavonol (V) has the characteristic properties of the group. When treated with *p*-benzo-quinone or quinhydrone it gives the gossypetone reaction forming a reddish brown quinone. It also exhibits prominent

157

R=R'=OH,R''=H, gossypin
R=OH, R'=R''=H, herbacetin
R=R''=OH, R'=H, hibiscetin
R=R''=R''=H, 8-hydroxy-galanga.

colour changes with alkaline buffer solutions. In regard to these colours there is a marked gradation from the lowest to the highest member of this group of flavonols. With hydroxy-galangin the violet colour is prominent and it diminishes in herbacetin[4] and gossypetin[5] and is absent in hibiscetin.[6] On the other hand, the pure and deep blue tone intensifies as the series is ascended. The stability of the flavonols in the solid state diminishes with increasing number of hydroxyl groups. Hydroxy-galangin retains its golden yellow colour almost indefinitely whereas hibiscetin becomes dark in a few weeks. A similar sequence is found in the melting points of the flavonols and of their important derivatives as shown in the following table :—

	Flavonol	Methyl ether	Acetate
Hydroxy-galangin ..	231–33°	155–58°	100–70°
Herbacetin ..	281–83°	167–58°	192–93°
Gossypetin ..	310° (decomp.)	170–72°	228–30°
Hibiscetin ..	360° (decomp)	194·96°	242–44°

EXPERIMENTAL

2 : 4-Dihydroxy-ω-3. 6-trimethoxy acetophenone (II).—This was prepared by the modified method of Rao, Rao and Seshadri [3]

7-Benzoyloxy-3. 5 : 8-trimethoxy flavone (III).—2 : 4-Dihydroxy-ω-3· 6-trimethoxy acetophenone (II) (2 g) was intimately mixed with sodium benzoate (10 g.) and benzoic anhydride (20 g.) and the mixture was heated under reduced pressure for four hours in an oil-bath at 175–80°. The mixture gradually shrank and partly melted down into a liquid. The reaction product was dissolved in boiling alcohol (150 c.c.), sodium hydroxide (6·5 g.) required just to neutralize the unreacted benzoic anhydride, was dissolved in 15 c.c. of water and this was added to the above boiling solution in small quantities during the course of 20 minutes. The mixture was then boiled under reflux for half an hour, and the solvent subsequently removed under reduced pressure. The residue, consisting essentially of the benzoyl-oxy compound, benzoic acid and its potassium salt, was macerated with dilute sodium carbonate solution. By this treatment benzoic acid and its salt went into solution leaving behind the benzoyloxy compound. It was filtered and recrystallised from a mixture of alcohol and acetic acid. It was thus obtained as colourless rhombic prisms melting at 185–87°, sintering a few degrees earlier. The yield was about 1·5 grams. (Found in the air-dried sample: C, 68·1; H, 5·1; $C_{25}H_{20}O_{7}$, $\frac{1}{2} H_2O$ requires C, 68·0; H, 4 8%.)

7-Hydroxy-3: 5 : 8-trimethoxy flavone (IV).—The benzoyl compound (III) was dissolved in boiling alcohol (100 c.c.) and treated with 10% potassium

hydroxide (10 c.c.) in small quantities during the course of 20 minutes. The mixture was then boiled under reflux for half an hour. The clear solution which was blue to litmus was cooled and the solvent removed under reduced pressure. The residue was treated with 50 c.c. of water and any undissolved impurity was removed by filtration. The clear alkaline solution was saturated with carbon dioxide when a crystalline yellow substance separated out in good yield. It was recrystallised from glacial acetic acid. When the crystallisation was carried out quickly, the substance came out as yellow rectangular plates and flat needles; by slow crystallisation, however, rectangular prisms were obtained The melting point was 236–38°. Yield 0·5 g. The substance was soluble in alkali and gave no characteristic colour with ferric chloride. (Found in the air-dried sample C, 64·1; H, 5·3; loss on drying at 120° *in vacuo* for 2 hours· 3·1; $C_{16}H_{16}O_6$ $\frac{1}{2}$ H_2O requires C, 64 1; H, 5·1; loss on drying, 2·7%.)

8-Hydroxy-Galangin (3·5 7:8-*Tetrahydroxy flavone*) (V) —7-Hydroxy-3:5:8-trimethoxy flavone (IV) (0·5 g) was dissolved in acetic anhydride (2 5 c.c.) and treated with hydriodic acid (10 c.c.) of 1·7 density The mixture was boiled under reflux for half an hour. After dilution with an equal amount of water, sulphur dioxide was passed through the solution in order to remove iodine. A yellow solid separated out in good yield. Direct crystallisation was not satisfactory. So the crude product was dissolved in dry ether and the solution treated with petroleum ether Some brown amorphous impurities were first precipitated and were removed. Further addition of petroleum ether gave hydroxy-galangin as a bright yellow crystalline solid. It was finally crystallised from alcohol when it came out as fibrous needles melting at 231–33° sintering a few degrees earlier (Found in the air-dried sample: C, 62·8; H, 3·9; $C_{15}H_{10}O_6$ requires C, 62·9; H, 3·5%.) There was no loss on drying at 120° *in vacuo* for two hours.

An alcoholic solution of the flavonol gave a deep red precipitate with neutral lead acetate and a brownish red colour with ferric chloride. The substance dissolved in concentrated sulphuric acid to form a yellow solution without fluorescence and dissolved in dilute alkali producing a purple solution which rapidly became yellowish-green on shaking.

The colour reactions of the flavonol in alkaline buffer solutions were as described below:

p_H 8·6. Rapidly dissolved to give a deep yellow solution. Slowly changed to violet (2 minutes) and then to bluish violet (10 minutes). The colour was stable for more than two hours. After twenty-four hours, the solution was colourless.

p_H 9·8. Dissolved immediately yielding a yellow solution which changed to violet and then to violet-blue within five minutes. The colour was fairly stable for two hours. After twenty-four hours the solution was colourless.

p_H 10·4. The initial yellow solution quickly changed to brown violet and then to violet. Within a minute, the solution was deep violet-blue which was stable for two hours; it was colourless after twenty-four hours.

p_H 11·0. Quick succession of changes: yellow, brown-violet, violet, deep violet-blue within half a minute. The colour was bluer than before. Stable for two hours but faded away within 24 hours.

By the action of *p*-benzoquinone in alcoholic solution the quinone derivative was obtained as a deep reddish brown solid which did not melt below 300° C. The tetra-acetyl derivative of the flavonol crystallised from alcohol in the form of colourless prismatic needles and melted at 169–70°.

7-Acetoxy-3 : 5 : 8-trimethoxyflavone 7-Hydroxy-3 : 5 : 8-trimethoxyflavone (IV) (0·2 g.) was acetylated using acetic anhydride and anhydrous sodium acetate. The acetyl derivative was sparingly soluble in alcohol. It crystallised from acetic acid as needles melting at 155–56°. (Found in the air-dried sample. C, 62·0; H, 5·5; loss on drying at 120° *in vacuo* for 2 hours, 4·2; $C_{20}H_{18}O_7$, H_2O requires C, 61·9; H, 5·2; loss on drying, 4·6%.)

3 : 5 : 7 : 8-Tetramethoxy flavone (VI).—7-Hydroxy-3 : 5. 8-trimethoxy flavone (IV) (0·2 g.) was dissolved in 20% sodium hydroxide (5 c c) and was treated with dimethyl sulphate (0·5 c.c.) added in drops with vigorous shaking. During this operation the methylated product began to separate out, but the reaction was brought to completion by heating the mixture on a water-bath for half an hour. On cooling, the methyl ether separated out completely. When recrystallised from dilute acetic acid, it was obtained as colourless woolly needles melting at 156–58° with sintering at about 100° (dehydration). (Found in air-dried sample: C, 60·5; H, 6·1; OCH_3, 31·9; $C_{19}H_{18}O_6$, $2H_2O$ requires C, 60·3; H, 5·8 and OCH_3, 32·8%. Found in the sample dried at 120° *in vacuo*: C, 66·2; H, 5·7; $C_{19}H_{18}O_6$ requires C, 66·7; H, 5·3%.)

Pentamethyl Herbacetin (VIII).—Herbacetin (2 g.) was dissolved in anhydrous acetone (50 c.c.); the solution was treated with anhydrous potassium carbonate (25 g.) and dimethyl sulphate (8 c.c.) and boiled under reflux for 30 hours. A further quantity of dimethyl sulphate (6 c.c.) was added in small quantities during the first 24 hours The mixture was finally filtered under suction while still hot and the residue was washed with a small quantity of hot anhydrous acetone. The filtrate was concentrated;

on the addition of excess of water the concentrate gave rise to a bulky precipi-
tate of the methylated flavonol. It was filtered and recrystallised from dilute
alcohol. Its crystal structure (fibrous needles) and melting point (156–58°)
were identical with the pentamethyl ether already described

2-*Hydroxy-ω-*3 : 4 : 6-*tetramethoxy acetophenone* (*Gossypetol-tetramethyl
ether*) (VII).—Pentamethyl herbacetin (VIII) (1 g.) was treated with absolute
alcoholic potash (2 g. of potash in 30 c.c. of absolute alcohol) and boiled
under reflux on a water-bath for about six hours. As much of the alcohol as
possible was then removed by distillation, the residue dissolved in water and
the solution acidified with excess of dilute sulphuric acid. The product was
then ether-extracted and the ether solution was washed repeatedly with 5%
sodium bicarbonate solution till no more acid could be extracted. The
solvent was then distilled off and the solid obtained was recrystallised from
dilute alcohol. It appeared as colourless flat needles melting at 115–16°.
Gossypetol-tetramethyl ether according to Perkin[7] has the same crystal
structure (needles) and melting point 115–16°.

The sodium bicarbonate washings were acidified and the acid that pre-
cipitated out was recrystallised from alcohol It was found to be identical
with anisic acid.

The ketone (gossypetol-tetramethyl ether) on condensation with benzoic
anhydride and sodium benzoate gave rise to 3 : 5 . 7- 8-tetramethoxy-
flavone identical with the sample prepared by the methylation of 7-hydroxy-
3 : 5 : 8-trimethoxy-flavone.

SUMMARY

8-Hydroxy-galangin, the lowest member of the gossypetin series of
flavonols, has been prepared and its properties and reactions compared with
the other members. Its important derivatives are described. The tetra-
methyl ether has been obtained by two methods, one of which is the direct
condensation of gossypetol-tetramethyl ether, obtained by the fission of
herbacetin pentamethyl ether, with benzoic anhydride and sodium benzoate.

REFERENCES

1.	Baker, Nodzu and Robinson		*J C S*, 1929, 74.
	Goldsworthy and Robinson		*Ibid*, 1937, 46
2	Rao. Rao and Seshadri	..	*Proc Ind Acad Sci*, A, 1943, 19, 88
3	Rangaswami, Rao and Seshadri		*Ibid*, 1939, 9, 133 ,
	Rao and Seshadri	.	*Curr Sci*, 1939, 6, 255
4	Neelakantam and Seshadri		*Proc. Ind Acad Sci*, A, 1937, 5, 362.
5	———, ——— and Rao	..	*Ibid.*, 1935, 2, 492
6.	Rao and Seshadri	..	*Ibid*, 1942, 15, 150.
7.	Perkin	..	*J. C. S.*, 1913, 653.

THE DIAMAGNETIC SUSCEPTIBILITIES OF SUCCINIC ACID AND SUCCINIC ANHYDRIDE

The Influence of the Anhydride Ring Structure on Molecular Diamagnetism

By Bawa Kartar Singh and K. Maghar Singh Manhas

(Department of Chemistry, University of Allahabad, Allahabad)

AND

Sunder Lal Agarwal, Noorul Haq and Mahan Singh

(Department of Chemistry, Government College, Lahore)

In an earlier communication,[1] it was shown that the magnetic suscepti-
bilities of camphoric acid and its anhydride followed Pascal's additivity
law, and that the difference in the values of their gram-molecular suscepti-
bilities was $- 13 \cdot 0 \times 10^{-6}$, which is just equal to the gram-molecular
susceptibility of water ($- 12 \cdot 96 \times 10^{-6}$). On the other hand, Gray and
Birse[2] found this difference to be $37 \cdot 0 \times 10^{-6}$, which was considerably
more than could be accounted for on the additivity law.

Gray and Birse[2] have also investigated succinic acid and its anhydride,
and have found that the difference in the values of their gram-molecular
susceptibilities, namely, $- 6 \cdot 9*$ is less than the gram-molecular suscepti-
bility of water. It was, therefore, considered desirable to redetermine the
magnetic susceptibilities of succinic acid and its anhydride Succinic an-
hydride is somewhat difficult to prepare in a pure condition, as it becomes
contaminated with the free acid during recrystallisation on account of the
presence of traces of moisture in the solvent, which brings about partial
hydrolysis. We have carried out the magnetic measurements on specially
purified material and find that the difference ($- 13 \cdot 6$) between the gram-
molecular susceptibilities of the acid and of its anhydride is nearly equal
to the gram-molecular susceptibility of water, in conformity with Pascal's
additivity law.

Pascal distinguishes three kinds of oxygen as regards its effective
atomic susceptibility: when it is singly bound to any two atoms as in alco-
hols and ethers, it is diamagnetic ($- 4 \cdot 61$); in ketones and aldehydes in

---

* The unit of magnetic susceptibility is taken throughout this paper as 10^{-6} c.g.s. e.m.u.

which it is doubly bound to a carbon atom, it is feebly paramagnetic ($+ 1 \cdot 71$); but when it is doubly bound to a single carbon atom, carrying another oxygen atom, it is again diamagnetic ($- 3 \cdot 71$). In acid anhydrides, the atomic susceptibility of the singly linked oxygen atom is the same as in alcohols and ethers: this follows from the concordance in the observed value of χ_M ($- 52 \cdot 73$) of acetic anhydride[3] with that calculated ($-52 \cdot 91$) on the basis of the singly linked oxygen atom being equal to $- 4 \cdot 61$.

Now it has been shown above that the difference in the gram-molecular susceptibilities of a dicarboxylic acid and its inner anhydride is equal to about $- 13$. But a dicarboxylic acid contains two atoms of hydrogen and one atom of singly linked oxygen more than the corresponding anhydride, and the sum of the susceptibilities of these three atoms, namely, $- 10 \cdot 47$, is numerically less than the above-mentioned difference. It, therefore, follows that the change of the acid into its anhydride produces a greater lowering in its diamagnetism than that which simply corresponds to two atoms of hydrogen and one of oxygen. The paramagnetic effect due to ring closure in the heterocyclic structure of an anhydride should, therefore, be equal to $- (- 12 \cdot 96 + 10 \cdot 47)$ or $+ 2 \cdot 53$. This, however, does not take into account any strain which may be associated with rings of different sizes. If the strain factor were absent, or in other words, rings of different sizes were equally stable, the paramagnetic value of the anhydride rings of different sizes would be the same, namely, $+ 2 \cdot 53$. It is, however, well known that the double bond between two carbon atoms (the ethylenic bond) and other types of unsaturated bonds are in a state of strain caused by the deflection of the carbon valencies from the tetrahedral angle of $109°, 28'$. The polymethylenes, according to the Strain theories,[4] are also in a similar state of strain, the amount of the strain depending on the number[†] of atoms and the nature of attached groups in the ring structure. Any deviation from the above-mentioned difference, $- 13 \cdot 0$, between the observed and the calculated values of χ_M of an acid and its anhydride will thus be a measure

---

† Baeyer's strain theory assumed that the carbon atoms of the ring must lie in a plane and on this basis rings containing six and more carbon atoms involved a negative strain, which was greater as the size of the ring increased This part of Bacyer's theory has now been discarded : Sachse[4] in 1890 first put forward the idea of stainless rings which was later elaborated by Mohr[4] and has recently been confirmed by experiment Since stable rings of as many as 32 carbon atoms are now known, there is no necessity of assuming a planar form for any ring of more than five members and the hypothesis of strainless rings of six and higher members in which the atoms forming the ring do not lie in a plane but must take up a multiplanar configuration has been widely adopted by chemists It should, however, be pointed out that there is evidence that some strain persists even in compounds containing very large rings.[5]

o the strain in rings of different sizes. This point is further elaborated in the discussion.

<center>EXPERIMENTAL</center>

Preparation of materials.—Succinic acid was purified by repeated crystallisation from hot water, when it was obtained as colourless prisms, m.p. 185° C.

Succinic anhydride was obtained by refluxing succinic acid with excess of acetyl chloride. It was then poured into a shallow dish and allowed to stand in a soda lime vacuum desiccator until acetyl chloride and acetic acid were cmpletely removed. It was recrystallised from absolute alcohol or anhydrous chloroform as long needles, m.p. 119–20°. It is essential that the solvent should be free from all traces of moisture, otherwise on re-crystallisation succinic anhydride is hydrolysed and the melting point falls.

Magnetic Measurements.—The magnetic susceptibility measurements were carried out on a modified form of Guoy's Balance The working of the balance was checked by making determinations of magnetic susceptibility of a few standard substances. The same procedure was followed with succinic acid and succinic anhydride. The results of these measurements are recorded in Table I

<center>TABLE I</center>

Substance	m.p.	$- \chi \times 10^6$ (per gram)	$- \chi_M \times 10^6$ (per gram molecule)	$- \chi_M \times 10^6$ (Gray and Bir e²)
Succinic acid	185°	0·487	57·47	54·45
Succinic anhydride	119–120°	(i) 0·438 (ii) 0·439	43 85	47 53
Difference	..	..	13·62	6·92

<center>DISCUSSION OF RESULTS</center>

The value of succinic acid, calculated on Pascal's additivity law from the atomic susceptibility of the elements, agrees with the experimental value:

Succinic Acid $\quad$ $CH_2.CO.OH$

$\qquad\qquad$ $\dot{C}H_2.CO.OH$, Mol. wt. = 118

χ_M (Calc.) $\quad = (4 C) + (6 H) + (2 O^\circ) + (2 - 0 -)$

$\qquad\qquad = - (24·00 + 17·58 + 6·72 + 9·22)$

$\qquad\qquad = - 57·52$

χ_M (Obs., Table I) $\quad = - 57·47$

$\qquad\qquad$ Deviation 0·1 per cent.

Succinic Anhydride,

$$\begin{array}{c} CH_2 \cdot CO \\ | \qquad\qquad\rangle O, \text{ Mol. wt} = 100 \\ CH_2 \cdot CO \end{array}$$
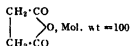
The sum of the atomic susceptibilities of four carbon, four hydrogen and three oxygen atoms, two of which have $(\chi_A)_0 = -3.36$ and one has $(\chi_A)_0 = -4.61$, is equal to -47.05 and is greater than the experimental value of $\chi_M = 43.85$ (Table I) by -3.2. The paramagnetic contribution of the 5-membered heterocyclic ring of the anhydride is, therefore, equal to $+3.2$. We have evaluated, as shown in the earlier part of this paper, the paramagnetic effect of anhydride rings as $+2.53$, provided no strain factor due to ring structure affecting magnetic susceptibility was involved. It may, therefore, be concluded from these magnetic measurements that the strain involved in the formation of the 5-membered ring in succinic anhydride is very small, as is to be expected.

Maleic anhydride

$$\begin{array}{c} CH - CO \\ | \qquad\qquad\rangle O, \text{ Mol. wt} = 98 \\ CH - CO \end{array}$$
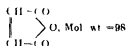
Similarly the calculated value of the susceptibility of maleic acid is -49.73, as against the observed value[2] -49.52, showing a very close agreement. On the other hand, the calculated value of maleic anhydride* agrees with the experimental value only when the effect of the ring-closure is taken into account. Here again the contribution for the ring comes out to be nearly the same as before, namely $+3.45$ as against $+3.2$ deduced for succinic anhydride. The small difference between the two values is probably within experimental errors. If genuine, it may be attributed to the extra strain due to the presence of a double bond in the ring of maleic anhydride, which is absent in the ring structure of succinic anhydride.

Camphoric Acid

$$\begin{array}{c} CH_2 \\ | \\ H_2C \!-\!\!-\!\!-\! C \!-\!\!-\!\!-\! COOH \\ | \qquad\quad H_3C \cdot C \cdot CH_3 \\ | \\ H_2C \!-\!\!-\!\!-\! CH \!-\! COOH \end{array}$$
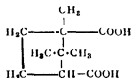

* The sum of the atomic susceptibilities of the elements (-41.19), the constitutive correction constant due to tertiary carbon atoms in relation to the two functional groups containing oxygen (-3.54) and the effect of the double bond $(+5.47)$ add up to -39.26 as against the observed value[2] of magnetic susceptibility -35.81, giving a paramagnetic effect of the ring as $+3.45$.

Similarly the molecular susceptibility of camphoric acid may be calculated on the basis of the additivity law, as follows:—

(a) Sum of the atomic susceptibilities of 10 carbon, 16 hydrogen and 4 oxygen atoms—2 of the oxygens are doubly bound and the other two singly bound = $-122 \cdot 74$

(b) Diamagnetic contribution of quaternary and tertiary carbon atoms on two* functional groups containing oxygen = $-6 \cdot 62$

(c) The contribution of the cyclopentano ring containing a *gem*-di-methyl group (λ) is obtained as $+4 \cdot 16$, when the sum of a, b and c factors is equated with the observed value[1] of gram-molecular susceptibility of camphoric acid ($-125 \cdot 2$)

It is found that in camphoric anhydride,
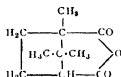
in order to get a fit between the calculated and the observed value[1] ($-112 \cdot 2$) of susceptibility, the effect of the six-membered heterocyclic ring, formed on passing from the acid into the anhydride, has to be taken as $+2 \cdot 61$,† which is nearly the same as in the other two anhydrides referred to above.

In Table II, the paramagnetic effect of the 5- and 6-membered anhydride rings is shown.

TABLE II

			Contribution due to the heterocyclic ring
1.	Succinic anhydride	(5-membered) ..	$+3 \cdot 2$
2.	Maleic anhydride	(5- ,,) ..	$+3 \cdot 45$
3.	Camphoric anhydride	(6- ,,) ..	$+2 \cdot 61$
			Mean $+3 \cdot 09$

* In a previous communication,[1] where a similar calculation was made, the effect of the tertiary and quaternary carbon atoms on only *one* of the two functional groups containing oxygen was taken into account. The neglect of the effect of the tertiary and quaternary carbon atoms on the other functional group and also of the effect of the cyclopentane ring, on the susceptibility, both due to oversight, almost cancel each other

† In a previous communication,[1] already referred to, it was stated that the ring closure in camphoric anhydride had no effect on its magnetic susceptibility, unlike on optical activity. This is not correct as the value of the paramagnetic effect ($+2 \cdot 61$) above calculated for the 6-membered anhydride ring shows. At the same time, it is to be admitted that whereas optical activity in camphoric anhydride is phenomenally depressed, ($\alpha = 0$), ring closure has not this marked effect on its susceptibility.

In calculating the value of the gram-molecular susceptibility of camphoric anhydride, the paramagnetic effect of the cyclopentane ring with a *gem*-dimethyl group ($+ 4 \cdot 16$) taken in the calculation was deduced from the susceptibility value of camphoric acid which also contains this ring. It may, however, be noted that it is lower than Pascal's value ($+ 7 \cdot 2$) for the cyclopentane series.

The observed differences in the gram-molecular susceptibilities of camphoric, maleic and succinic acids and their corresponding anhydrides are given in Table III.

TABLE III

	$- x_M \times 10^6$	Difference
Camphoric acid[1]	125·20	12·95
Camphoric anhydride[1]	112·25	
Maleic acid[2]	49·52	13·71
Maleic anhydride[2]	35·81	
Succinic acid (Table I)	57·47	13·62
Succinic anhydride (Table I)	43·85	

We thus see that the observed difference between the susceptibilities of dicarboxylic acids and the corresponding anhydrides, which in all the three cases is nearly equal to the susceptibility of water ($- 13 \cdot 0$), can be explained on the additivity law, if the anhydride ring is taken to contribute about $+ 3$ to the molecular susceptibility. The small varia'ion in this contribution observed in the different anhydrides is well within experimental error, and is also of the same order as may be expected from the different amounts of strain in the rings in the three anhydrides.

SUMMARY

(1) Measurements have been made on the magnetic susceptibilities of succinic acid and its anhydride.

The susceptibilities are:

$$x_M = - 57 \cdot 47 \times 10^{-6} \text{ for the acid;}$$
$$x_M = - 43 \cdot 85 \times 10^{-6} \text{ for the anhydride.}$$

(2) The difference between the gram-molecular susceptibilities of succinic acid and its anhydride is that of a molecule of water.. This is to be expected, both from considerations based on the additivity law, and from observations on other acids and their anhydrides, namely camphoric acid, maleic acid and their corresponding anhydrides.

(3) The difference of about 13 is numerically more than can be attributed to two atoms of hydrogen and one of singly linked oxygen, which will give only 10·47.

(4) The extra effect is attributed to the formation of a ring in the anhydride, the paramagnetic contribution of which may be taken as about + 2·5.

REFERENCES

1	Singh, B K, Agarwal, S L, and Singh, M	*Proc Nat Acad Sci*, A, 1944, **14**, 72
2.	Gray, F W, and Birse, W M	*J Chem Soc*, 1914, **105**, 2707
3		Pascal's value as given in *International Critical Tables*, 1929, **6**, 361.
4	Baeyer, A	*Ber*, 1885, **18**, 2277.
	Sachse	*Ibid*, 1890, **23**, 1363 ; *Zeit physikal chem*, 1892, **10**, 203.
	Mohr	*J prakt chem*, 1918, (2) **98**, 349 , 1922, **103**, 316
	Beesley, R M , Ingold, C K , and Thorpe, J F	*J Chem Soc*, 1915, **105**, 1080.
	Baker, J. W , and Ingold, C K	*Ibid*, 1923, **123**, 122
	Ingold, C K , and Thorpe, J F	*Ibid*, 1928, 1318
5	Carothers, W H , and Hill, J. W	*J Am Chem Soc*, 1933, **55**, 5043

STUDIES ON THE NATURE OF THE RACEMIC MODIFICATION OF OPTICALLY ACTIVE COMPOUNDS

Part IV. Roozeboom Solubility-Composition Isotherm for Mixtures of Active and Inactive Camphor-β-Sulphonic Acids at 35°

By Bawa Kartar Singh and Onkar Nath Perti

(Department of Chemistry, University of Allahabad)

INTRODUCTION

In Part I of this series[1] it was proposed to undertake the phase rule study of the nature of the racemic modification of optically active compounds according to Roozeboom's Solubility Method.[2] In the present communication the racemic form of camphor-β-sulphonic acid has been studied by this method.

The racemic modification can occur in three forms, viz., (i) a mixture of the two optically active and opposite forms in equal proportions (conglomerate), or (ii) a compound of these two forms, or (iii) a solid solution of the dextro and lævo forms in equal proportion due to the enantiomorphs being isomorphous, each crystal containing both the forms. The solid solution differs from the conglomerate in constituting a single phase.

The existence of racemic compounds in the solid state is well known.[3] But the evidence for the existence of racemic compounds in the liquid state is very meagre. The problem was attacked by Ladenburg[4] who found that a lowering of temperature occurred when d- and l-coniine were mixed whereas no change in temperature was observed in the case of certain other liquids of a similar character having similar specific gravity. From these facts he argued that d- and l-coniine unite to form a racemic compound in the liquid state, and suggested that change of temperature on mixing the two enantiomorphs would indicate the existence of a racemic liquid, but such a view has been shown to be untenable.[5] The ordinary cryoscopic method gives molecular weights of the racemic forms identical with those of the active forms,[6] showing the absence of racemates in solution. Bruni, however, found that the molecular weight increased on the addition of one of the active forms. Similar investigations on electrolytic conductivity,[7] molecular volume,[8] surface tension,[9] and molecular refraction[10] did not yield any positive evidence for the existence of racemic compounds in the liquid state or in solution. On the other hand, Stewart[11] observed that the absorption spectra of the active and racemic forms of tartaric acid gave indication

170

of the existence of racemic compound at concentrations above 14%. One of us[12] had studied the viscosity of solutions of *d-*, *l-* and *dl-* forms of camphor and some of its derivatives at different concentrations. A comparison of the viscosity values of the three forms at corresponding concentrations showed that the values for all the three were identical upto a certain concentration only but above this concentration though the values for *d-* and *l-* agreed, those of the *dl-* form were appreciably higher indicating the existence of racemic compounds in solution at these higher concentrations. Again, one of us[13] had also investigated the pharmacological action of *d-*, *l-* and *dl-*forms of sodio-isonitroso-camphor and camphor-β-sulphonic acid and their aniline and toluidine salts in solution. In the case of the latter substances, their toxicity to the paramœcia, effect on the central nervous system, action on frog's heart and effect on the plain muscles of the intestines and uterus, were examined. It was found that the effects of *d-*, *l-* and *dl-*forms were different. When the effect of the racemic form is highest or lowest of the three modifications the conclusion is drawn that it is a true *dl-*compound. In this way it was shown that the racemic forms of camphor-β-sulphonic acid and its aniline and toluidine salts are true *dl-*compounds in solution. As a result of these pharmacological experiments a Biochemical Method has thus been developed for determining the nature of the racemic modification. The results of this Biochemical Method are in agreement with the conclusions drawn from Roozeboom's Freezing-Point Method.[1]

Solubility relationships which should exist between optical enantiomorphs, racemic mixtures, racemic compounds and racemic solid solutions have been discussed from the point of view of the phase rule by Roozeboom[2] and Bruni.[14] Roozeboom's reasoning is as follows: the addition of a solid fusible phase lowers the freezing-point of an organic compound; similarly, the presence of a second soluble phase alters its solubility. Hence, if a solubility-composition isotherm of a racemic modification with its dextro and lævo isomers is plotted, a racemic mixture should give two curves, a racemic solid solution one curve and a racemic compound three curves.

So far as the present authors are aware no actual solubility-composition isotherms of optically active and racemic forms are known, nor is there any experimental data available which definitely correlate the mixed freezing-point or melting-point curves with the above mentioned solubility curves. The present paper deals with the solubility measurements on camphor-β-sulphonic acids* at 35° in water.

A4

EXPERIMENTAL

The *l*- and *dl*-camphor-β-sulphonic acids were prepared in the same way as Reychler's acid[1] (*d*-camphor-β-sulphonic acid).

First the solubility of pure *d*-, *l*- and racemic forms was determined separately. The substance in excess together with conductivity water was put in a small ground glass stoppered bottle, the neck of which was covered by a piece of India rubber tied tightly round it by means of a string. This bottle was placed in a mechanical device attached to the stirrer of a thermostat. The stirrer was rotated by an electric motor and the temperature of the bath maintained at 35° ± 0 05° by a toluene regulator. After saturation had reached, approximately 1 to 2 c.c. of the saturated solution was sucked by means of a warm pipette having a glass tube filled with glasswool attached to the end. The amount of the racemic form was determined by titration with alkali and that of the optically active form by polarimeter. In the case of solubility of mixtures, one form was first completely dissolved and then the solution was saturated with the other form in excess. In this way by gradually altering the concentration of the former a series of solubility measurements of the mixtures were made. The amount of the active form in the saturated solution was estimated polarimetrically and the total quantity of acid by titration. Beyond a certain concentration of the mixed acids, the solution became too viscous to be sucked out with the above mentioned pipette.

DISCUSSION

The experimental results are recorded in Tables I and II and represented graphically in Figs. 1 and 2. Fig. 1 is plotted with the total solubility (gm. per 100 gm. of the solvent) as ordinates and the percentage composition as abscissæ. Fig. 2 is plotted according to Stokes-Roozeboom method for three component systems, the amount of solute being expressed as gm. per 100 gm. of solution. Since *d*- and *l*-isomers behave in identical ways for properties of a scalar nature[16] the solubility-composition isotherm will be symmetrical, one half being the mirror image of the other. The half diagram corresponding to the solubility of mixtures of the *l*-form and the racemic modification (indicated by dotted lines) was drawn as the mirror image of the other half corresponding to the solubility of the mixtures of the *d*-form and the racemic modification. The five points representing five solubility measurements with the *l*-form fit in exactly on this dotted curve (*vide* Figs 1 and 2).

The invariant points (0, 0') could not be determined experimentally: the solution after a certain concentration of the total acid becomes too

TABLE I   (*cf.* Fig. 1)

Solubility of mixtures of optically active and racemic forms of
camphor-β-sulphonic acid in gms. per 100 gms. of water at 35°

Total solubility in gms./100 gms. water (By titration)	% of d or l- (By polarimeter)	% of dl- (By difference)	Solid phase in excess
316·7	100 d	0	
321·2	92·48 d-	7·52	d acid
329·9	87·13 d-	12 87	
339·9	82·99 d-	17 01	
Solution becomes too viscous to carry on solubility determinations			
334·8	61·00 d-	39·00	
323·8	55·21 d	44 79	
296·0	39·04 d	60·96	
288·4	30·32 d-	69·68	
278·5	21·23 d	78·77	dl-acid
271·9	11·49 d-	88·51	
266·1	0 d-	100	
289·4	33·86 l	66·14	
325·0	57·97 l-	42·03	
334·9	—	14·77	
325·5	85·23 l	11·45	l-acid
314·4	88·55 l-	0	
	100 l-		

TABLE II   (*cf.* Fig. 2)

Solubility of mixtures of optically active and racemic* forms of
camphor-β-sulphonic acids per 100 gms. of solution at 35°.

Amounts in gms. present in 100 gms. of solution			Solid phase in excess
Water	d-	l	
24·00	76·00	0	
23·74	73·40	2·86	d-acid
23·26	71·80	4·94	
22·74	70·69	6·57	
Solution becomes too viscous to carry on solubility determinations			
23·00	61·98	15·02	
23·60	59·29	17·11	
25·25	51·97	22·78	
25·75	48·38	25·87	
26·42	44·60	28·98	dl-
26·88	40·76	32·36	
27·34	36·33	36·33	
25·65	24 86	49·49	
23·53	16·07	60·40	
22·99	5·69	71·32	
23·50	4·38	72·12	l acid
24·15	0	75·85	

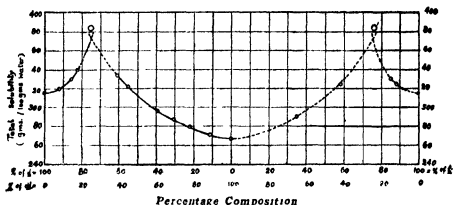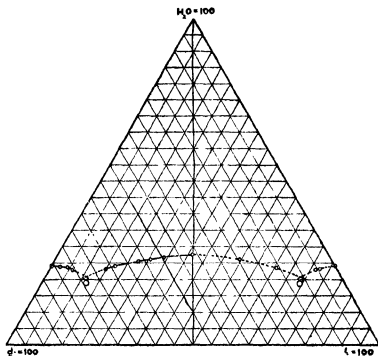* *dl*-Acid has been split up into components, *d-* + *l*-acid, in the table.

Fig 1

Fig 2

viscous to carry on further measurements. The number of points determined, however, was sufficient to indicate the general nature of the curves and the invariant points (0, 0') were obtained by extrapolation (dotted extensions in Figs. 1 and 2).

A study of Figs. 1 and 2 shows that in each case three curves are obtained, indicating that the racemic form of camphor-β-sulphonic acid is a true *dl*-compound at 35°.

The nature of the racemic modification of camphor-β-sulphonic acid was previously studied by us[17] by Roozeboom's Freezing-point (actually melting-point) Method. The results indicated that at the temperature of melting, the racemic form was a *dl*-compound. Comparison of the mixed melting-point diagram[17] and the mixed solubility diagram (Fig. 1) shows that the general nature of these curves is very similar except that whereas the composition of the eutectic point of the melting-point-composition curve is 30 *dl*-: 70 *d*-, that of the invariant point of the solubility-composition isotherm at 35° is 24 *dl*-: 76 *d*- (or *l*-), (by extrapolation from graph).*

Suppose that at the temperature at which the nature of the racemic modification is determined, the racemic compound is partly dissociated into the *d*- or *l*-forms. It is obvious that the greater the dissociation the less would be the alteration in solubility or melting-point when either *d*- or *l*-form is added to the racemic modification. In other words, the flatness or otherwise of the diagram would depend upon the extent to which the racemic form is dissociated into the active forms and may be taken as a measure of the degree of dissociation of the racemic modification. The slope of the curve (Fig. 1) is steep which indicates that the amount of dissociation of the racemic camphor-β-sulphonic acid is fairly small. From the study of both the melting point-composition diagram[17] and the solubility-composition isotherm (Fig. 1) it is evident that in each of these cases the middle portion forms the greater part of the diagram, indicating that the *dl*-camphor-β-sulphonic acid is very stable both in the fused and in the dissolved state.

PHYSICAL IDENTITY OF ENANTIOMERS

According to Pasteur's principle of Molecular Dissymetry the *d*- and *l*-forms should possess identical physical properties as regards their magnitude. The solubility determinations described in the present paper further support this principle. It is found that not only the solubilities of *d*- and *l*-forms at 35° are identical but also the solubility-composition isotherms of *d*- and *dl*-, and *l*- and *dl*- are exact mirror images of one another (*vide* Figs. 1 and 2).

---

* The extrapolated value of the composition of the invariant point 0 (or 0′) as deduced from Stokes-Roozeboom diagram is water : *d*- (or *l*-) : *dl*- as 21 : 58 : 21.

176   Bawa Kartar Singh and Onkar Nath Perti   .

SUMMARY

(1) The solubility-composition isotherm for camphor-β-sulphonic acids
at 35° has been determined and shown to consist of three curves indicating
that the racemic modification is a true dl-compound.

(2) The solubilities of d- and l-camphor-β-sulphonic acids are equal
at 35°.

(3) The shape of the melting-point-composition diagram and the
solubility-composition isotherm enables us to infer that dl-camphor-β-
sulphonic acid is stable and its range of stability is large.

REFERENCES

1. Singh, B K , and Perti, O N   Proc Nat Acad Sci India, 1943, 13, 59.
2. Roozeboom   .. Ber., 1899, 32, 557; Zeit. Physik. Chem,
                           1899, 28, 494
? Centnerzwer   Zeit. Physik Chem , 1899, 29, 715 ;
  Adriani   Ibid , 1899, A 2, 462 et seq ,
  Astbury, W T.   Proc Roy Soc , 1923, 104, 219 ,
  Ross and Somerville .   Jour Chem. Soc , 1926, 2770 ;
  Singh, B K , and Perti, O N   Proc Nat Acad Sci India, 1943, 13, 59 ,
                           1944, 14 A, 79
4 Ladenburg   .   Ber , 1895, 28, 163, 1991.
5 Adriani   Zeit Physik Chem , 1900, 53, 453.
6 Raoult   .   Ibid , 1889, 3, 372
7 Ostwald   Ibid , 1889, 3, 372 ,
  Walden, P.   Ber , 1896, 29, 1692
8 Marchlewski   Ibid , 1892, 25, 1556
9 Mitchell, A D , and Smith, C   Jour Chem Soc , 1913, 103, 489 ,
  Smith, C   Ibid , 1914, 105, 1703
10 Pope and Peachey   .   Ibid , 1899, 75, 1111
11 Stewart, A W   .. Ibid , 1907, 91, 1386.
12 Singh, B K , et al   Proc. Ind Acad Sci , 1937, 5, 484.
13 Singh, B K , and Prasad, S   .   Ibid , 1936, 3, 586 ,
  Bhatia, B B , Singh, B K , et al   Proc. Nat Acad Sci India, 1944, 14 B, 171
14. Bruni   .   Gazz chim Ital , 1900, 30, 35.
15 Reychler   Bull , 1898, (III), 19, 120.
16 Pasteur   .   Oeuvres, 66 ; A. C P , 1884, (III), 24, 443.
   Singh, B K , et al .   Jour. Ind Chem. Soc , 1930, 7, 771, et seq
17. Singh, B. K , and Perti, O N   .   Proc. Nat. Acad Sci. India, 1944, 14 A, 79.

MAHADEVITE—A NEW SPECIES OF MICA

By S. RAMASESHAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

1. INTRODUCTION

" DURING the regular geological survey of the ' Bison hill range ' (Eastern Ghats) to the south of the Godavari, in the eastern parts of Warangal district in the month of February 1944 (20th Feb. 1944), sheets of bronze-coloured mica, up to about $18'' \times 14''$ were found in a pegmatite vein which cuts through a band of micaceous schists in the Khondalites (sillimanite-garnet gneiss). Almost parallel to the band of micaceous schists in this area, there are persistent runs of crystalline limestones. The sheets of mica occur on the flank of a hill called ' Racha Konda ' (Lat. $17°\ 28'$ long. $81°\ 20'$) at an elevation of about 500 ft. above the bed of the Godavari (*i.e.*) at about 650 ft. M.S.L. It was discovered almost at the surface in the pegmatite vein, and a trial pit to a depth of about 10 ft. showed a thick pocket of the mica amidst these pegmatites ".

The above is reproduced from a note by Prof. C. Mahadevan, now of the Andhra University, of a find made by him during his work as an Officer of the Hyderabad State Geological Survey. A few sheets of the mica were sent by him to Sir C. V. Raman and the examination of the same by both physical and chemical means was entrusted to the present writer. It was found that the properties and composition of the mica were different from those of the usual varieties (*i.e.*, muscovite, phlogopite and biotite). The differences are so marked as to justify its recognition as a new species of mica, the name of the discoverer being associated with it.

The mica has the usual vitreous lustre and thick sheets of it are bronze-coloured and are practically opaque. Thin flakes of about 1 mm., however, are transparent and exhibit a greenish yellow hue. The cleavage is highly perfect, producing thin elastic laminæ. Mention must be made of the fact that the transparency, pliability and homogeneity of the flakes preclude the possibility of the mica being considered an altered or decomposed product.

The pleochroism in this mica is definitely more than that in muscovite but is much less than that in biotite. Like all micas, this specimen is optically negative and the acute bisectrix is practically normal to the plane of

cleavage. The optic axial angle as measured in air, *i.e.,* 2 E, is 13° 48'. **This value approximates to that in phlogopite and biotite but is much less than that in muscovite.**

A six-rayed percussion figure can be easily obtained in a cleavage plate of the mica by striking it with a sharp pointed instrument. It is well known that in micas the most prominent of the rays is parallel to the clino-pinacoid or the plane of symmetry. The above method was used for determining the plane of symmetry of the mica. The interference figures formed by convergent polarised light show that the plane of the optic axes (*i.e.,* the plane containing the two melatropes) is at right angles to the plane of symmetry. In muscovite and some exceptional biotites (called anomites) the plane of the optic axes is perpendicular to the plane of symmetry. Thus, the mica under study resembles muscovite as far as the orientation of the optic axial plane is concerned. Thus the physical characteristics of Prof. Mahadevan's mica do not fit in with those of the usual micas.

2. CHEMICAL ANALYSIS

A complete chemical analysis of the mica was undertaken and the methods adopted were those advocated by Washington (1910). A small sheet of mica free from any inclusions was ground well in an agate mortar and about 0·5 gm. of the powder was mixed with 5 gms. of sodium carbonate and fused in a platinum crucible. When the fusion was complete, the mass was extracted with dilute hydrochloric acid. When the fusion was complete, the mass by evaporating the solution to dryness. Silica is filtered off and in the filtrate alumina and iron oxides (ferrous oxide being converted into ferric by oxidation with bromine water) are precipitated with ammonia water in the presence of excess of ammonium chloride. The precipitate is ignited and weighed and brought into solution by fusion with potassium pyrosulphate. The melt is dissolved in water and ferric iron is reduced by granulate zinc and the total iron is determined by titration against potassium permanganate solution.

The filtrate from ammonia precipitation is precipitated with ammonium oxalate. The precipitate of calcium oxalate is dissolved and reprecipitated and lime determined by titrating the solution of calcium oxalate in dilute sulphuric acid against potassium permanganate solution.

In the filtrate from calcium oxalate, magnesia is determined by precipitation as ammonium magnesium phosphate which after solution and reprecipitation is ignited and magnesia weighed as pyrophosphate.

The alkalies are determined by the Lawrence-Smith method and the combined water by the Penfield method. No attempt was made to estimate

the individual alkalies present. All the necessary precautions against undue errors creeping in were taken. The value obtained for alumina may be too high because no attempt was made to determine the TiO₂ present.

Three different samples were analysed independently and the results of two are given in Table I. Table I also contains typical results of analyses of other varieties of mica. The values for anomite are those of Tschermak (1879).

TABLE I

Name		SiO₂	Al₂O₃	Fe₂O₃	FeO	MgO	CaO	Na₂O	K₂O	H₂O	Others	Total
Mahadevite—												
Analysis	I .	38·98	29·94	4·12		13·2	0·49	9·6		3·8	.	100·13
Analysis	II .	38·34	29·20	3·86		14·4	0·50	9·2		3·8	..	99·20
Muscovite	I ..	45·57	36·72	0·05	1·28	0·38	0·21	0·62	8·81	5·05	0·34	99·93
„	II .	43·47	36·70	2·10	0·55	..	..	1·95	8·57	5·50	0·35	99·59
Phlogopite	I ..	39·66	17·00	0·27	0·20	26·49	..	0·60	9·97	2·99	3·42	100·80
„	II ..	42·56	12·18	2·73	0·90	22·40	0·20	0·44	10·70	2·35	6·20	100·66
Biotite	I ..	32·49	12·34	6·56	25·13	5·29	..	0·88	9·59	2·42	5·64	100·34
„	II ..	36·75	14·70	4·65	14·08	12·37	0·17	0·32	9·19	4·67	4·	99·9
Anomite	I ..	40·00	17·28	0·72	4·88	23·91	..	1·47	8·57	1·97	1·60	100·00
„	II ..	40·84	16·47	2·16	5·92	21·08	..	1·55	9·01	2·19	..	99·22

3. PLACE IN THE SCHEME OF MICAS

A study of Table I shows that the specimen has too much magnesium oxide to be muscovite, too little iron to be biotite and too much alumina to be phlogopite. The fact that the mica has a low optic axial angle and that it has the plane of the optic axes perpendicular to the plane of symmetry may lead one to the conclusion that the mica is similar to the anomites described by Tschermak (*loc. cit*). The enormous differences in the chemical-composition of the two varieties is sufficient proof to show that such a conclusion is wrong. A search of the literature [Hintze (1897), Dana (1911), etc.] has failed to reveal any mica or altered mica (such as steatite, serpentine, etc.) having approximately this composition.

Micas exhibit a bewildering variation of chemical composition and many attempts have been made to explain this variation (Iddings, 1911). The most successful and useful theory is that put forward by Pauling (1930). According to him, the structure of mica consists of two sheets of hexagonal net-work of linked SiO₄ tetrahedra placed with vertices pointing inwards. These vertices are cross-linked by Al atoms in muscovite and by Mg and Fe atoms in phlogopite and biotite. (OH) groups are linked to Al, Mg and Fe alone. The structure is a succession of such double sheets with K and Na atoms placed between them. In this structure, Al can replace Si forming

aluminium-oxygen tetrahedra ; Al, Mg and Fe occupy positions of six co-ordination and K, Na, Ca, etc. are in positions of 12 co-ordinations. Mauguin (1928) has suggested that instead of taking continuous chemical substitution, the number of atoms in a unit cell (a) forming linked tetra-hedra, (b) in 6 co-ordination position and (c) in 12 co-ordination position should only be considered.

Mauguin's analysis shows that the number of oxygen atoms in the structural unit (which is ¼ of the unit cell) is always twelve within errors of analysis. Assuming this fact, the number of atoms of different elements in the structural unit of the mica under investigation has been calculated.

TABLE II*

		Biotite	Muscovite	Phlogopite	Anomite	Mahadevite
I	O	11·85	11·99	12·2	12·0	12·0
	F	0·0	0·03	0·0	..	..
	O + F	11·85	12·02	12 2	12·0	12·0
II	Si	2·80	3·00	2·79	2 95	2·68
	Al	1·17	1·00	1 21	1·05	1·32
	Si + Al	4	4	4	4	4
III	Al	..	1·84	0·28	0·45	1·10
	Fe	0·4	0 05	⎱ 0·14 ⎰	0·35	0 20
	Fe	0·8	0·07			
	Mg	1·49	0·04	2·60	2·60	1·36
	Others	0·09	0·05	0 00	..	..
	No. of atoms in 6 co ordination	2 78	2·05	3·06	3·40	2·66
IV	Ca	..	0·01	.	..	0·04
	Na	0·06	0·08	⎱ 0·12 ⎰	..	0·93
	K	1·07	0·74	0·94	1·018	
	No of atoms 12 co ordination	1·13	0·83	1·06	1·018	0·97
V	H	1·75	2 20	2·08	0·66	1·73

* The values for biotite, muscovite and phlogopite have been obtained from *Atomic Structure of Minerals* by W L Bragg, 1937, p 213 The values for anomite have been calculated from Tschermak's analysis.

Table II shows the number of atoms of different elements in the struc-tural unit of the well-known varieties of mica and the specimen under study. The atoms have been divided into 4 groups. The first consists of fluorine and oxygen atoms and the second contains Si with sufficient Al atoms to make the total in this group equal to four. This represents the Si and Al in sheets of linked tetrahedra. The next group consists of atoms in positions of six co-ordination and the fourth of atoms in positions of twelve co-ordi-nation.

The study of Table II shows that the total number of atoms in position of six co-ordination in the new mica is nearly the same as that in biotite but larger than that in muscovite. If one considers the numbers of atoms of the individual elements in the 6 co-ordination position, it is found that they do not fit in with any of the known varieties. One can say that in a general way the values lie midway between those for muscovite and phlogopite. In muscovite, there is a large proportion of aluminium and very little of magne-sium, while the reverse is the case with phlogopite. In the present specimen, the two elements occur to nearly the same extent.

It may be remarked that while a continuous variation in the relative proportions of iron and magnesium has been noticed (Clarke, 1924), the partial replacement of magnesium by aluminium is not so common. In particular, the relative proportion of approximately 1 : 1 of the Al and Mg atoms in six co-ordination found in the present mica has never been observed before.

In conclusion, the author wishes to express his thanks to Prof. Sir C. V. Raman for his guidance during this investigation.

SUMMARY

The physical properties and chemical composition of a species of mica from the Warangal district in Hyderabad have been studied. Thick sheets are bronze-coloured and opaque, while thin sheets transmit light of a green-ish yellow tint, the pleochroism being weakly but distinct. The optic axial angle is 13° 48'. Th plane of the optic axes is perpendicular to the plane of symmetry. The composition is SiO_2 38·98%, Al_2O_3 29·94%, Fe_2O_3 and FeO 4·12%, Mgo 13·2%, K_2O 9·6% water 3·8%. On the basis of Pauling's model of the mica structure, the numbers of atoms of various elements in six, and twelve co-ordination positions are calculated. Approximately equal number of Al and Mg atoms are found in six co-ordination. The mica appears to be of a type intermediate between muscovite and phlogopite.

REFERENCES

Clarke, F. W.	*The Data of Geochemistry*, 1924, 395.
Dana	*A system of Mineralogy*, 1911, 611
Hintze, C.	*Handbuch der Mineralogie*, 1897, **2**, 515.
Iddings, J. P.	*Rock Minerals*, 1911, 448
Mauguin, C.	*Comptes Rendus*, 1927, **185**, 288 ; 1928, **186**, 79 and 1131
Pauling, L	*Proc. Nat. Acad Sciences*, 1930, **16**, 123
Tschermak, G.	*Zeit. fur Kristallographie*, 1879, **3**, 132.
Washington, H. S.	*Manual of Chemical Analysis of Rocks*, 1910.

RAMAN SPECTRA OF THE SECOND ORDER IN CRYSTALS

Part I: Calcite

By R. S. KRISHNAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received 23rd September 1945

1. INTRODUCTION

The Importance of the Second Order Raman Effect.—It is well known that in the Raman spectra of certain substances, for example BF., CCl$_4$, etc., a few fainter lines are recorded, the frequency shifts of which cannot be identified with fundamental vibration frequencies of the molecule. These shifts have therefore been sought to be explained as octaves or combinations of the fundamental vibration frequencies. From theoretical considerations, Placzek (1934) showed that the appearance of the first overtone of every normal oscillation of a molecule is allowed in the Raman effect irrespective of whether it is permitted or forbidden as a fundamental. On the assumption that the molecule is a linear harmonic oscillator, Placzek attributed the appearance of overtone lines to the fact that the variations of optical polarisability are not directly proportional to the displacements, and hence the second order derivative of the polarisability with respect to the normal co-ordinate cannot be neglected. Later, Bhagavantam (1939) showed that even if the second order term was neglected, overtone lines would still appear with a finite intensity on account of the fact that all molecules should really be treated as anharmonic oscillators. He calculated the relative intensities of the fundamental and overtone Raman lines for a few diatomic molecules. Even after taking into consideration the anharmonicity and the finite value of the second order derivative of polarisability, the theory shows that the overtone and combinational lines are ordinarily very weak compared with the fundamentals. Hence to record them the use of intense sources and of long exposures is necessary. The extra effort is, however, worth while since the knowledge of the frequency shifts and of the intensities with which these lines are recorded, gives us valuable additional information regarding the dynamical and optical properties of the molecules.

Precisely the same considerations that are detailed above apply also in the case of crystals. There is, however, a further interest attaching to the

study of the second order spectra of crystals. According to the Raman dynamics of crystal lattices, (Raman, 1943) every crystal has in addition to the $(3p - 3)$ modes of internal oscillations of the group of p non-equivalent atoms contained in the unit cell, $21p$ more modes of oscillation of the lattice in which the equivalent atoms in adjacent cells vibrate in opposite phases. By their very nature, these $21p$ modes are inactive as fundamentals in light-scattering, and hence they can only manifest themselves as octaves or combinations in the second order Raman effect.

Technique of Study.—As already remarked, it is essential to employ a monochromatic light source which is very intense for recording the second order frequency shifts. It is also of great importance that there should be no continuous spectrum accompanying the same. This is secured by using the 2536·5 A.U. mercury resonance radiation from a water-cooled magnet-controlled quartz arc. The enormously increased scattering power of the resonance radiation arising from its exceptional intensity as compared with the other mercury radiations and from the λ^{-4} law has made it an ideal source for Raman effect studies in the case of crystals that are transparent to the ultra-violet and do not get coloured by prolonged exposure to this radiation. The 2536·5 A.U. radiation from the light scattered by the medium is effectively suppressed before its entry into the spectrograph by absorption in a column of mercury vapour, as otherwise the photographic plate would be fogged. This makes it possible to record faint Raman lines with small frequency shifts on a clear background. Rasetti (1929) was the first to use this technique for the study of the Raman effect in gases and crystals. He did not, however, push the technique to the limit of its usefulness. The power of the Rasetti technique can be judged from the fact that by employing the same the author (Krishnan, 1944) succeeded in recording the Raman spectrum of the second order in diamond and obtained results affording a direct experimental verification of the predictions of the Raman theory of crystal dynamics.

Using the technique described in the previous paragraph, a systematic investigation of the Raman spectra of the second order in various crystals has been undertaken. This paper which is first of a series deals with the results obtained with calcite together with a brief review of the previous work on the Raman effect in calcite.

2. Previous Work on Calcite

Next to quartz, calcite has been the crystal most frequently examined in Raman effect studies. Most of the earlier work on the subject was confined to the cataloguing the frequency shifts of the lines and estimating their

relative intensities, *viz.*, Landsberg and Mandelstam (1928), Wood (1928), Kimura and Uchida (1928), Krishnan (1929), Nisi (1929, 1932), Schaefer, Matossi and Aderhold (1929, 1930), Venkatesachar and Sibaiya (1930), Rasetti (1931) and Tomaschek (1931) On the whole, seven Raman lines with frequency shifts 155, 221, 282, 709, 1084, 1434 and 1749 cm.$^{-1}$ and two anti-Stokes lines corresponding to 155 and 282 cm.$^{-1}$ have been reported. The line with frequency shift of 221 cm.$^{-1}$ is reported only by a few investigators. The line at 1749 cm.$^{-1}$ has been assigned as the overtone of the infra-red active, Raman inactive fundamental frequency at 879 cm.$^{-1}$ So far, this is the only second order Raman line that has been definitely observed in calcite.

Besides measuring the frequency shifts and relative intensities, Kimura and Uchida (1929) studied the variations in intensity of the Raman lines in calcite for various orientations of the crystal. Cabannes (1929, 1933), Daure (1929), Matossi (1930), Cabannes and Osborne (1931) and Michalke (1938) investigated the state of polarisation of the Raman lines using incident unpolarised light for various orientations of the crystal. Miss Osborne (1932), Bhagavantam (1939, 1940) and Bhagavantam and Rao (1940) on the other hand, made a detailed study of the relative intensities and depolarisation of the Raman lines of calcite for various orientations of the optic axis and the important result emerging out of these investigations is the reciprocal behaviour of the lattice oscillations on the one hand and the total symmetric oscillation on the other. Bhagavantam has given a satisfactory explanation of the results by studying in detail the character table, Bhagavantam and Venkatarayudu (1939), and the selection rules, Bhagavantam (1941), for calcite.

The influence of temperature on the intensity, frequency shift and width of the Raman lines in calcite, has been studied by Ornstein and Went (1935) over the range of temperature from 90°K to 423° K, by Kopcewicz (1937) over the range from 293°K, to 683° K, and by Venkateswarlu (1942) from 305° K to 493° K. The main results obtained by them can be summarised in the following words. The ratio of the intensities of the Stokes to the anti-Stokes line is found to obey the modified Boltzmann formula throughout the range of temperature investigated. There is a decrease of intensity with increase of temperature which is more rapid in the case of the low frequency or lattice lines than for internal lines corresponding to the oscillations of the CO_3 group. The lattice lines with frequency shifts 155 and 282 cm.$^{-1}$ exhibit marked shifts towards the exciting line and an appreciable broadening with increase of temperature the width being proportional to

the square root of the absolute temperature, whereas the lines due to the internal oscillations and especially the symmetric oscillation with frequency shift 1084 cm.$^{-1}$ are practically unaffected by variations of temperature over the range investigated.

Some miscellaneous investigations have also been reported in the literature concerning the Raman effect in calcite. Embirikos (1930) reported that the frequencies of the CO_3 group are higher in the calcite crystal than in solution of carbonates. A comparative study of the Raman spectra of calcite and aragonite was made by Bhagavantam (1931) who concluded that the CO_3 group retained the same structure in both. A similar comparative study of the Raman spectra of calcite and sodium nitrate without reference to directional excitation was made by Cabannes and Canals (1931) and more recently by Sundara Rama Rao (1939) Ornstein and Went (1935) investigated the dependence of the intensity of Raman lines in calcite on the wavelength of the exciting line. They reported that the increase in intensity of the lines was more rapid than to be expected on the basis of the fourth power law as the wavelength of the exciting line was decreased.

By adopting a set of seven force constants, four of which pertain to the forces of the free ion and the remaining three to the inter-ionic forces in the crystal and giving appropriate numerical values for the same, Bhagavantam and Sundara Rama Rao (1944) have evaluated the frequencies of oscillation of calcite and compared the same with those observed in Raman effect and infra-red absorption.

3. DETAILS OF THE EXPERIMENT

In all the earlier investigations on the Raman effect in calcite except the one by Rasetti (1931), the 4046 A.U. and 4358 A.U. radiations of the mercury arc were used for exciting the Raman spectrum. The technique of using these radiations as exciter has already been exploited to the limit of its utility and it is rather unlikely that any further useful information regarding the second order Raman spectrum of calcite would be got by adopting the same. In the present investigation, the well-known Rasetti technique which consisted in the use of the 2536·5 A.U. resonance radiation, has been employed.

The details of the construction and the running of the quartz mercury arc specially designed for the emission of the resonance radiation with an exceptional intensity have already been described by the author in an earlier paper (Krishnan, 1944). A transparent crystal of calcite $2'' \times 2'' \times 1\frac{1}{4}''$ and a smaller specimen of size $\frac{3}{4}'' \times \frac{3}{4}'' \times \frac{1}{4}''$ were chosen for the present

investigation from Sir C. V. Raman's personal collection. The specimen was usually mounted with one of its flat faces in front of the most intense portion of the arc. The transversely scattered light was taken through one of its edges and was condensed on the slit of a quartz spectrograph. A column of mercury vapour was introduced in the path of the scattered light to suppress the 2536·5 A.U line. The crystal was cooled by means of a fan.

Two different instruments were used for photographing the Raman spectrum of calcite; (1) A Hilger E1 quartz spectrograph which has a dispersion of about 50 wavenumbers/mm. in the 2536 region; and (2) a Hilger E3 quartz spectrograph which is relatively fast and has a dispersion of about 140 cm.$^{-1}$/mm. in the same region. The higher dispersion instrument was used in order to measure the frequency shifts and widths of the principal Raman lines very accurately. Using a very fine slit (0·01 mm.) and the smaller crystal, exposures of the order of 24 hours were given to photograph the Raman spectrum of the first order with reasonable intensity.

The smaller instrument was used to get an intense photograph of the Raman spectrum of calcite showing the second order lines. With this instrument and using the bigger crystal, the first order Raman lines could be photographed in a couple of minutes using a slit width of 0·03 mm. Exposures varying from 12 to 48 hours were given to get an intense spectrogram.

The negatives were measured under a Hilger cross-slide micrometer.

4. RESULTS

First Order Raman Spectrum.—The frequency shifts together with the widths of the first order or fundamental Raman lines as measured from the spectrogram taken with the high dispersion instrument are given in Table I. The values reported earlier by Cabannes and Osborne and by Rasetti are also included in the same table.

TABLE I. *Raman Spectrum of the First Order in Calcite*

	Lattice Oscillation		Internal Oscillation		
	E_2	E_g	E_g	A_1	E_g
	Cm.$^{-1}$	Cm.$^{-1}$	Cm.$^{-1}$	Cm.$^{-1}$	Cm.$^{-1}$
Author	155·5	283·9	711·8	1085·6	1433·8
	(7·5)	(10·5)	(3·0)	(5·5)	(3·5)
	[8]	[15]	[2]	[20]	[5]
Cabannes and Osborne	157·5	283·8	712·1	1087·3	1436·6
Rasetti	155·7	283	713·8	1087·6	1436·7

The figures enclosed in ( ) represent the widths of the lines in wave numbers, while those given in square brackets represent the relative peak intensities of the lines on an arbitrary scale. As the slit width used was very narrow and the spectrogram was very lightly exposed, the widths of the lines given in Table I are considered genuine and not due to photographic broadening. The temperature of the crystal which was slightly above the room temperature, would have wandered by five degrees either way. The finite width of the lines may be responsible for the descrepancies in the values of the frequency shifts given by the author and those reported by the earlier investigators. The anti-Stokes Raman lines corresponding to 155·5, 283·8, 711·8 and 1085·6 cm.⁻¹ have been clearly recorded in the spectrum of the scattered light.

Second Order Spectrum.—A heavily exposed spectrogram taken with the E3 spectrograph is reproduced in Fig 1 together with a photograph of the direct arc. The microphotometric record of the same is reproduced in Fig. 2. The second-order Raman lines are clearly seen on the microphotometric record. They can also be identified on the reproduced photograph. Their positions as well as the frequency shifts have been marked in both the figures. In addition to the five intense principal lines belonging to the first order spectrum, there are not less than eleven Raman lines of comparatively feeble intensity belonging to the second order spectrum. Of these, nine lines have been recorded for the first time. The frequency shifts of these lines have been measured and are listed in Table II. The line with the frequency shift of 1750 cm.⁻¹ should naturally be the most intense one, as is evident from the fact that most of the earlier investigators who worked in the visible region have invariably recorded a line with the same frequency shift. With the 2536·5 A.U. excitation, this modified line falls in the region of the Hg triplet at 2652·0, 2653·7 and 2655·1 A.U. A comparative study of the two depressions in the microphotometric record of the mercury triplet with the corresponding ones of the direct arc shows that the Raman line actually falls in the region between the Hg lines at 2653·7 and 2655·1 A.U. The frequency shifts of this line have therefore been taken as 1750 cm.⁻¹, this being the mean of the separations in wave-number of the two mercury lines from the exciting line, namely 2536·5 A.U.

The principal Raman line at 1085·6 cm.⁻¹ corresponding to the total symmetric oscillation has a companion to the left with a frequency shift of 1065 cm.⁻¹ It is too intense and too near the main line to be assigned as arising from the total symmetric oscillation excited by the mercury line λ 2534·8 A.U.

A5

The lines with frequency shifts 2147 and 2172·5 cm.⁻¹ form a close doublet and come next in order of intensity. They stand out prominently in the spectrum. The former is comparatively broad and shows a subsidiary maximum at about 2130 cm.⁻¹, while the latter is sharp.

The existence of a feeble line with a frequency shift of 221 cm.⁻¹ was reported by some of the earlier investigators. This has been confirmed by the author The Raman bands with mean frequency shifts 2220 cm.⁻¹ and 2310 cm.⁻¹ are rather broad and diffuse. The former one has a width of about 40 cm.⁻¹ with the peak intensity displaced towards the left, while the latter has a width of 30 wavenumbers and is more or less of uniform intensity throughout.

The Raman line at 864 cm.⁻¹ unfortunately falls close to a faint mercury line. A critical examination of the two photographs reproduced in Fig. 1, shows that in the spectrum of the scattered light, the line in this region appears to be broad, while in the mercury arc spectrum it is definitely sharper The microphotometric record shows the line at 864 cm ⁻¹ clearly resolved from the faint mercury line on the longer wavelength side.

The remaining three second order Raman lines are weak in intensity. They are easily discernible in the microphotometric record.

The heavily exposed spectrum of the scattered light in calcite shows the presence of a feeble continuum on either side of the exciting line and extending up to about 300 cm ⁻¹ from it. The intensity of the continuum at any point is definitely less than one hundredth part of the intensity of the weakest of the first order Raman lines.

It will be noticed from the microphotometric records reproduced in Fig 2 that the intensity of the 2536·5 A.U. line relative to that of its companion at 2534·8 A U. is greater in the spectrum of the scattered light than in that of the direct arc, although the same column of mercury vapour was used in both cases. This can be explained as due to the fact that in the so-called unmodified scattered radiation there are also Brillouin components which arise from the reflection of the incident radiation by the standing elastic waves inside the crystal. These components have a finite though small wave number separation from the unmodified line and are hence not absorbed by the column of mercury vapour. By. using instruments with high resolving power, it should be possible to record the Brillouin components clearly separated from the unmodified line.

Close to and on the left side of the mercury line at 2675·0 A. U. there is a Raman line. As the separation of this line from the strongest of the

TABLE II. *Second order Raman spectrum of calcite*

Serial No	Measured frequency shifts in cm⁻¹	Assignment	Calculated frequency shifts in cm⁻¹	Observed frequency shifts in infra-red absorption
1	221	2 E_1 (l)	108 + 106	..
2	864	E_2 (l) + E_2 (l)	712 + 156	..
3	1065	B_1 (l) + b_1 (i)	357 + 706	.
4	1360	A_1 + E_2 (l)	1086 + 284	1358
5	1583	B_1 (i) + F_1 (l)	879 + 706	1586
6	1750	2 B_1 (i)	879 + 879	1735
7	(2130)*	E_1 (i) + E_1 (i)	706 + 1430	..
	2147	F_1 (i) + E_2 (i)	712 + 1434	2155
8	2172·5	2 A_1	1086 + 1086	..
9	2220	B_1 (i) + E_1 (i)	879 + 1350	2220
10	2310	B_1 (i) + F_1 (i)	879 + 1430	..
11	2500	A_1 + E_2 (i)	1086 + 1434	2545

(l) signifies internal oscillation and (l) lattice oscillation   * The figure given in brackets represents the frequency shift of the subsidiary maximum of the broad line at 2147 cm⁻¹

mercury triplet in the 2650 A. U. region corresponds to the frequency shift of the stronger of the two lattice lines, it is assigned, as a first order Raman shift 284 cm⁻¹ excited by mercury line λ 2652·0 A. U.

Rasetti (1931) had reported the existence of a group of lines with frequency shifts from 7270·3 to 7455·5 cm⁻¹ for calcite. In the spectrum of the mercury arc which was kept continuously evacuated by an ordinary Cenco pump, there were a host of nitrogen lines falling approximately in the same region and hence it was not possible to prove or disprove the existence of the lines with these high frequency shifts. The point will be examined in detail later.

5. DISCUSSION OF RESULTS

A complete group-theoretical analysis of the normal modes of oscillation of the calcite lattice has been carried out by Bhagavantam and Venkatarayudu (1939), taking the unit cell containing two molecules of $CaCO_3$ as the repeating unit in the dynamic crystal. The main results obtained by them are summarised in Table III. The four distinct normal modes of the CO_3 ion in solution splits up into eight internal modes in the crystal. The doubling arises from the fact that the basis contains more than one *free* ion. The distribution of the eight modes among the various classes is shown in Table III.

<center>R. S. Krishnan</center>

<center>TABLE III</center>

Class	n_l	n_i	Raman	Infra-red	Observed frequencies Lattice cm⁻¹	Observed frequencies Internal cm⁻¹
A_1	0	1	P	f		1086
A_2	2	1	f	f		
B_1	2	1	f	P	106, 357	879
B_2	1	1	f	f		
E_1	3	2	f	P	106, 182, 330	706, 1350–1430
E_2	2	2	P	f	156, 284	712, 1434

n_l = No. of distinct modes belonging to lattice oscillations r_i No. of distinct modes of belonging to internal oscillations   P = Permitted to appear   f = forbidden

The notations have the usual significance as understood in group theo-
retical analysis. There are on the whole ten lattice frequencies, five single
and five doubly degenerate. They are also listed in the table. The ana-
lysis shows that those oscillations belonging to the internal group or to the
lattice group that are active in the Raman effect, should be inactive in infra-
red absorption and vice versa. Consequently there will not be any exact
coincidence between the Raman and infra-red absorption frequencies. The
infra-red absorption and reflection of calcite has been studied by numerous
investigators (refer to the Bibliography at the end of the paper) and some
of the results are summarised by Schæfer and Matossi (1930). The observed
frequencies are 106, 182, 330 and 357 cm⁻¹ belonging to lattice group and
706, 879 and 1350–1430 cm⁻¹ belonging to the internal group. The
observed Raman and infra-red frequencies are classified in Table III

Applying the usual selection rules, it is easily seen that in the second
order Raman spectrum the overtones of all the fundamental frequencies
and also the following combinations, namely $A_1 + E_2$, $E_1 + B_1$, any two
E_1s and 2 E_2s can appear. Those combinations, one component of
which belongs to either class A_2 or B_2 which is inactive in both, are neglected.
It should be pointed out that all overtones and combinations that are
allowed will not necessarily be recorded in the spectrum as some of them
may be too faint to be observed.

On the basis of the above selection rules, satisfactory assignments have
been given to most of the lines appearing in the second order Raman
spectrum, see Table II. The calculated frequency shifts agree reasonably well
with the observed lines. The corresponding combinational frequencies
observed in infra-red absorption are also included in Table II for purposes
of comparison. The two broad bands with mean frequency shifts of 2220
and 2310 cm⁻¹ have been assigned as the combinations of the infra-red

active, Raman inactive fundamental frequency at 879 cm^{-1} coming under class B_1, with doublet frequencies reported in infra-red absorption in the region of $7\,\mu$ coming under class E_1. The values given for the two frequencies are very varied. I have taken them as 1350 cm.$^{-1}$ and 1430 cm.$^{-1}$.

It is important to point out that the octaves of the intense lattice lines which appear as fundamentals with frequency shifts 156 and 284 cm^{-1} do not appear in the Raman spectrum Only the octaves of the far infra-red reststrahlen frequency of calcite which is at 106 cm.$^{-1}$ and which comes under class B_1, is recorded as a Raman line at 221 cm^{-1} in the second order spectrum. The octave of another infra-red frequency at 357 cm.$^{-1}$ which is also coming under class B_1 (lattice) even if present, would fall on the principal Raman line at 712 cm^{-1}. The extreme feebleness of other second order lattice lines and consequent difficulty in recording the same are to be attributed to the fact that calcite is an ionic crystal, and the changes of polarisability involved in lattice oscillations should necessarily be very small. This explains why none of the ($2lp$) super lattice oscillations that are contemplated on the basis of the Raman dynamics of crystal lattices, in which the atoms in the neighbouring cells vibrate in opposite phases, is recorded either as an octave or as a combination in the second order Raman spectrum.

The author wishes to thank Professor Sir C. V. Raman for the loan of the calcite crystals and for his kind interest in the work.

6. Summary

The importance of the study of the second order Raman spectra in crystals for getting a deeper insight into dynamical and optical properties of crystals has been pointed out.

The previous work on the Raman effect in calcite has been briefly reviewed.

Using the 2536·5 A.U. mercury resonance radiation, the first and second order Raman spectra of calcite have been photographed. As has already been reported the first order spectrum consists of five lines. The frequency shifts and widths of these lines have been accurately measured.

The second order spectrum exhibits a series of eleven lines of varying intensity and width. The frequency shifts of these lines are 221, 864, 1065, 1360, 1583, 1750, 2147, 2172·5, 2220, 2310 and 2500 cm.$^{-1}$. Some of these appear also in the infra-red absorption spectrum of calcite with very nearly the same freequncies. On the basis of the group theoretical analysis given

A6

by Bhagavantam, the observed second order Raman lines have been assigned
as some of the octaves and allowed combinations of the fundamental fre-
quencies of vibration of the calcite lattice.

The existence of Brillouin components along with the unmodified
radiation in the light scattered by the crystal of calcite has been demonstrated
in a very simple way.

A complete bibliography on the Raman effect and infra-red studies in
calcite is also included.

REFERENCES

1 Introductory

Placzek	*Handbuch der Radiologie*, 1934, **Bd. 6**, Teil II.
Bhagavantam	*Proc. Ind Acad Sci.*, A, 1939, **10**, 224.
Raman	. *Ibid.*, 1943, **18**, 237.
Rasetti	*Phys Rev*, 1929, **34**, 367.
Krishnan, R. S.	. *Proc. Ind. Acad Sci.*, 1944, **19**, 298.

2. Raman Effect

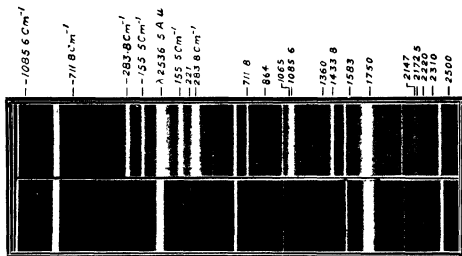|	
Landsberg and Mandelstam	*Comp. Rend.*, 1928, **187**, 109 ; *Naturwissenschaften*, 1928, **16**, 557 ; *Zeit. f Phys*, 1928, **50**, 769.
Wood, R W.	*Phil Mag*, 1928, **6**, 729.
Kimura and Uchida	*Jap. Journ Phys*, 1928, **5**, 97.
Krishnan, K. S	. *Ind. Journ Phys.*, 1929, **4**, 131.
Nisi	. *Proc Imp Acad Tokyo*, 1929. **5**, 127.
Schæfer, Matossi and Aderhold	*Phys. Zeits.*, 1929, **30**, 581.
——————	*Zets. f Phys*, 1930, **65**, 289 —
Venkatesachar and Sibaiya	.. *Ind. Journ. Phys.*, 1930, **5**, 747.
Rasetti, F.	*Nature*, 1931, **127**, 626 ; *Nuovo Cimento*, 1932, **9**, 72.
Tomaschek	*Nature*, 1931, **128**, 495.
Nisi	.. *Proc. Phys Math. Soc. Japan*, 1932, **14**, 214.
Kimura and Uchida	*Sci. Papers Ins. Phys. & Chem. Japen*, 1929, **11**, 199.
Cabannes	*Comp Rend*, 1929, **188**, 1041 ; 1933, **196**, 977.
Daure	. *Ann de Phys.*, 1929, **12**, 375.
Matossi	. *Zeits. f. Phys.*, 1930, **64**, 34
Cabannes and Osborne	*Comp Rend*, 1931, **193**, 156.
Michalke, H.	.. *Zeits f. Phys*, 1938, **108**, 748.
Osborne	.. *Diss., Paris*, 1932.
Bhagavantam, S	. *Curr Sci*, 1939, **8**, 507 ; *Proc. Ind. Acad. Sci.*, 1940, **11**, 62.
—————— and Rao, B. P.	.. *Curr Sci.*, 1940, **9**, 409.
—————— and Venkatarayudu	. *Proc. Ind. Acad. Sci.*, A, 1939, **9**, 224.
Bhagavantam	.. *Ibid.*, 1941, **13**, 543.
Ornstein and Went	: *Physica*, 1935, **2**, 503.

Fig. 1   (a) Raman spectrum of calcite
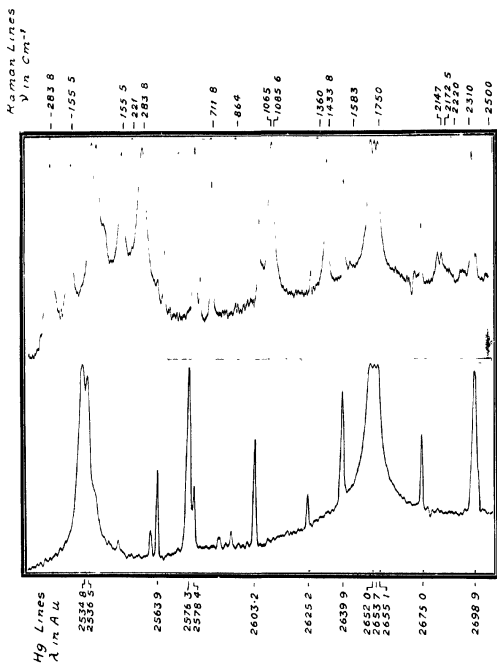
(b) Mercury spectrum

Fig. 2 Microphotometric records (a) Raman spectrum of calcite

(b) Mercury spectrum

Went	..	*Doctorate Thesis*, Utrecht, 1935
Kopcewicz	.	*Journ. de Phys., et Radium* 1937, **8**, 6.
Venkateswarlu	.	*Proc. Ind Acad Sci.*, A, 1942, **16**, 45
Embirikos	.	*Zeits. f. Phys.*, 1930, **65**, 266.
Bhagavantam	..	*Zeits f Kristal* , 1931, **77**, 43
Cabannes and Canal		*Comp. Rend* , 1931, **193**, 289
Sundara Rama Rao	.	*Proc Ind Acad Sci.*, A, 1939, **10**, 167.
Ornstein and Went	.	*Physica*, 1935, **2**, 391
Bhagavantam and Sundara Rama Rao		*Curr Sci* , 1944, **13**, 12

3. *Infra-red*

Merrit, E.		*Wied Ann* , 1895, **55**, 49.
Nyswander, E. R.	.	*Phys. Rev.*, 1908, **26**, 539 , 1909, **28**, 291
Rubens, H.	.	*Verhandl Deut. Physik Ges.*, 1911, **13**, 102.
Schæfer, C., and Schubert		*Ann der Phys* , 1916, **50**, 283
Liebisch T , and Rubens, H.		*Sitz Preuss Akad Wiss.*, 1919, 198
Rusch, M.		*Ann der Phys* , 1923, **70**, 373
Schæfer, C., Matossi, F , and Bormuth		*Zeit f Phys* , 1926, **39**, 648
Plyler, E. K.	.	*Phys Rev.*, 1927, **29**, 923 , *Science*, 1927, **65**, 578.
Schæfer, Matossi and Dane		*Zeit. f Phys* , 1927, **45**, 493
Matossi and Dane		*Ibid* , 1927, **45**, 501
Matossi, F.		*Ibid* , 1928, **48**, 616
Nielson, H. H.	..	*Phys Rev* , 1928, **32**, 773.
Taylor, A. M.	..	*Phil Mag* , 1928, **6**, 88
Randall and Nielson	.	*Phys. Rev* , 1928, **31**, 1131.
Plyler, E K.	.	*Ibid.*, 1929, **33**, 948
Schæfer, C.	..	*Zeit f Phys* , 1929, **54**, 676
Ellis, J. W.		*Proc Nat Acad Sci* , U S , 1930, **16**, 315.
Silverman, S.	..	*Phys. Rev.*, 1932, **39**, 72
Matossi, F.		*Phys. Zeits* , 1933, **34**, 230
——— and Brix, H.	..	*Zeit f Phys* , 1934, **92**, 303
Schæfer, C., and Matossi, F.	.	*Das Ultrarote Spektrum*, 1930.

ELASTIC CONSTANTS OF GARNETS

By B. RAMACHANDRA RAO

(From the Department of Physics, Andhra University, Guntur)

Received July 31, 1945

(Communicated by Prof S Bhagavantam, F.A.Sc.)

1. INTRODUCTION

ELASTIC behaviour is an important aspect of crystal physics. In view of their availability in large and well-developed forms, garnets are chosen for study in this paper and examined for their elastic behaviour. The fact that they crystallise in the cubic system makes the investigation quite simple.

2 STRUCTURE AND COMPOSITION OF GARNETS

It is a very well-known fact that garnets form a series of isomorphous crystals all belonging to the cubic system. The predominant habit is the dodecahedron. X-ray analysis has shown that they belong to the space group O_h^{10} which is the last in the list of 230 space groups. There are 8 molecules per unit cell and the side of the cube varies from $11 \cdot 50\,\text{Å}$ and $12 \cdot 02\,\text{Å}$. Chemical analysis of garnets has shown that they can be represented by the general formula $R_3 R_2 (Si\,O_4)_3$ where $\dot{R} = Ca$, Mg, Fe, Mn, $\dot{R} = Al$, Fe, Cr. They are of widely variable composition, the chief constituents of which are given below:—

		Density	Lattice constant in Å°
Pyrope	$Mg_3\ Al_2\ (Si\ O_4)_3$	3·51	11·51
Grossularite	$Ca_3\ Al_2\ (Si\ O_4)_3$	3·53	11·83
Uvarovite	$Ca_3\ Cr_2\ (Si\ O_4)_3$	3·77	11·95
Andradite	$Ca_3\ Fe_2\ (Si\ O_4)_3$	3·84	12·92
Spessartite	$Mn_3\ Al_2\ (Si\ O_4)_3$	4·18	11·60
Almandite	$Fe_3\ Al_2\ (Si\ O_4)_3$	4·33	11·50

All existing garnets are invariably isomorphous mixtures of the above in all possible proportions. On account of this fact colour, hardness, refractive index, specific gravity and other physical properties vary widely from specimen to specimen.

In all garnets quartz is invariably present as small inclusions. These inclusions are randomly distributed so that sections cut with different

194

orientations but from the same mother crystal sometimes show slight variations in density. Hence in the following investigations the densities of the various sections are determined separately and used in the respective calculations.

3. THEORETICAL CONSIDERATIONS

The elastic constants for the cubic system are given by the following scheme:

$$
\begin{matrix}
C_{11} & C_{12} & C_{12} & O & O & O \\
 & C_{11} & C_{12} & O & O & O \\
 & & C_{11} & O & O & O \\
 & & & C_{44} & O & O \\
 & & & & C_{44} & O \\
 & & & & & C_{44}
\end{matrix}
$$

The velocities of propagation of sound waves in a direction (l, m, n) in a cubic crystal are given by the roots of the equation[1]:

$$
\begin{vmatrix}
C_{11}l^2 + C_{44}(m^2 + n^2) & (C_{12} + C_{44})lm & (C_{12} + C_{44})nl \\
\quad - \rho c^2 & & \\
(C_{12} + C_{44})ml & C_{11}m^2 + C_{44}(l^2 + n^2) & (C_{12} + C_{44})mn \\
 & \quad - \rho c^2 & \\
(C_{12} + C_{44})nl & (C_{12} + C_{44})mn & C_{11}n^2 + C_{44}(l^2 + m^2) \\
 & & \quad - \rho c^2
\end{vmatrix} = 0
$$

Specialising this equation for the specific cases of propagation of sound in directions perpendicular to (100), (110) and (111) faces, we have the solutions given below:

TABLE I

Orientation of the plate	$v_1^2 \rho$	$v_2^2 \rho$	$v_3^2 \rho$
100	C_{11}	C_{44}	C_{44}
110	$\dfrac{C_{11} + C_{12} + 2C_{44}}{2}$	C_{44}	$\dfrac{C_{11} - C_{12}}{2}$
111	$\dfrac{C_{11} + 2C_{12} + 4C_{44}}{3}$	$\dfrac{C_{11} - C_{12} + C_{44}}{3}$	$\dfrac{C_{11} - C_{12} + C_{44}}{3}$

where $v_1^2 \rho$ corresponds to a longitudinal wave and $v_2^2 \rho$ and $v_3^2 \rho$ to shear waves.

The experimentally determined values of $v_1^2 \rho$ in different cases are equated to the appropriate expressions given in Table I and hence the principal elastic constants calculated for each specimen.

4. Experimental Determinations

In this series of investigations seven different specimens are used. Two of them, numbered six and seven in Table II are of the semi-precious variety. All the crystals used were of the dodecahedral habits with well-developed faces and free from twinning From these crystals, sections parallel to the cube faces (100), the natural faces (110) and the octahedral faces (111) are cut and employed in the measurements. The (100) and (111) sections are obtained to the accuracy of a contact goniometer.

Ide[2] has recently measured the Young's modulus of a number of rock-forming minerals both by static and by dynamic methods and found that the dynamic values are always about 10% higher than the static ones. Theoretically the difference between the dynamic and static measurements cannot be expected to be more than about 0·30%.[3] This large difference is attributed by him to the non-homogeneity of the material and the possible existence of cracks which invariably give low values by static methods. Hence in studying the garnets it is always preferable to use dynamic methods.

Recently Bhagavantam and Bhimasenachar[4] have described a new method applicable to such substances. This new method has been employed in the present investigation. All the garnets studied showed cracks which precluded the application of static methods. Results of these determinations are given in Table II.

Table II

Elastic Constants of Garnets and their Composition

Properties of Garnets \ No.	1	2	3	4	5	6	7
Density in gm per c.c	3·759	3·673	3·630	3·67	3·75	4·13	4·32
Elastic constants in dynes/cm² ×10⁻¹²							
C_{11}	1·97	1·92	2·10	2·22	2·26	2·73	3·27
C_{12}	0·90	0·99	1·03	1·04	1·26	1·57	1·24
C_{44}	0·57	0·59	0·87	0·70	0·62	0·68	0·89
Bulk modulus K ×10⁻¹²	1·26	1 30	1 39	1·43	1·60	1·62	1·90
Composition (percentage of FeO)	21· 8	22·7	23·6	23·0	26·2	28·7	33·5
Compressibility in cm.²/dynes ×10¹²	0·79	0·77	0·72	0·69	0·63	0·62	0·52

In the table, the bulk modulus K is calculated from the well-known relation $K = (C_{11} + 2C_{12})/3$. The garnets have been chemically analysed. Standard methods of analysis have been used and their ferrous content determined.

5. DISCUSSION OF RESULTS

From Table II we see that the elastic constants vary from specimen to specimen. In spite of the large variations in the principal constants, it is interesting to note that the bulk modulus K is directly proportional to the ferrous content of the specimen. This is clearly brought out by the curve of Fig. 1. It may be noted here that the points for the specimens 4 and 5
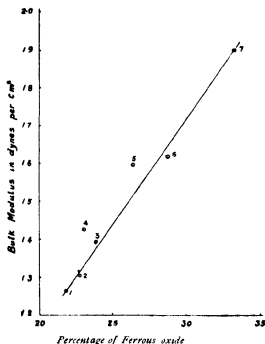

Percentage of Ferrous oxide

FIG 1

fall a little outside the curve. This may be due to the fact that the chemical method has not permitted us to estimate the ferric iron and it is possible that in these two specimens there is an excess of ferric iron. This is borne out by the fact that both these points fall on the left side of the curve.

We may mention here that Adams and Gibson[5] have determined the compressibilities of two varieties of garnets by using piezometric methods. They give a value of 0.60×10^{-12} cm.²/dyne for the compressibility of almandite. In our measurements specimen No. 7 which contains about 80% of almandite shows a compressibility of 0.52×10^{-12} cm.²/dyne. The agreement may be regarded as very satisfactory in view of the existing differences in composition and the well-known fact that piezometric values are usually high in consequence of the inherent difficulties of the method.

198   B. Ramachandra Rao

    Finally it may be remarked that the curve given above can be used for
an estimation of almandite in garnets provided the spessartite content is low.

                              6. SUMMARY

    Employing   the   new   method   developed   by   Bhagavantam   and
Bhimasenachar, elastic constants of seven specimens of garnets have been
determined. It has been found that the principal elastic constants show a
large variation from specimen to specimen. Nevertheless the bulk modulus
is found to vary linearly with the iron content.

    Finally the author wishes to express his grateful thanks to
Prof. S. Bhagavantam, HON D SC , for his keen interest and guidance during
the work. The author is also indebted to the Syndicate of the Andhra
University for the award of a Research Fellowship.

                             REFERENCES

    1   Bhagavantam, S , and   Proc Ind Acad Sci , 1944, 20, 304
        Suryanarayana, D

    2   Ide, J M   Proc Nat Acad Sci , 1936, 22, 81, 482

    3   Jaquerod, A , and Zuber, O Helv Physica Acta , 1932, 5, 438

    4   Bhagavantam, S , and   Proc Ind Acad Sci , 1944, 20, 298
        Bhimasenachar, J

    5   Adams, L H , and Gibson,   Proc Nat Acad Sci , 1929, 15, 713
        R. E

ELASTIC CONSTANTS OF CALCITE AND SODIUM NITRATE

BY J. BHIMASENACHAR

(From the Department of Physics, Andhra University, Guntur)

1. NATURE OF THE BINDING FORCES

CALCITE and sodium nitrate are two substances whose physical properties have been investigated thoroughly. Their specific heat and thermal expansion have been known from a long time.[1] The infra-red[2] and Raman spectra[3] have been studied in great detail. X-ray analysis[4] has revealed their internal structure. The dielectric constants[1] have been studied and measurements have been made over a wide range of frequencies. The magnetic anisotropies[5] have been studied with great care. In spite of this wealth of information it has not been possible to definitely establish the nature of the binding forces.

Firstly X-ray analysis shows that the interatomic distances are such as to compel us to regard the structures as ionic. On the other hand, it is well known to workers on Raman effect that ionic substances do not show strong Raman lines and even when a weak Raman spectrum is studied it is usually the overtone lines that make their appearance. Both these substances show a strong Raman effect. Further these two crystals show a strong dielectric depolarization which should not be expected if they were ionic structures. This has led different schools of workers to postulate different types of force fields.

Chapman, Topping and Morall[6] have calculated the potential energy of calcite series of carbonates assuming an electrostatic force field. Lennard-Jones and Dent[7] have calculated the potential energy due to the repulsive forces between the various atoms and combined it with the results of Chapman *et al.* and have successfully explained the cell size and other parameters. In a similar manner Topping and Chapman[8] have analysed and successfully explained the structure constants of sodium nitrate.

On the other hand, Bhagavantam and Venkatarayudu[9] have employed group theoretical methods and analysed the vibration spectra of the substances and successfully accounted for their infra-red and Raman spectra. These authors have used a valence force field. Continuing the work of these authors, Sundara Rama Rao[10] has introduced further refinements in the

valence force field and has explained even the structure details of the infra-
red and Raman lines.

In view of the intimate connection that exists between the elastic con-
stants and the force field it was felt that it is necessary to investigate the
elastic behaviour of these substances. Calcite has already been studied
thoroughly by Voigt,[11] but sodium nitrate has not yet been studied fully.
Hence both these crystals have been taken up for a thorough examination.

2. CHOICE OF CRYSTAL SECTIONS AND SOLUTIONS OF
CHRISTOFFEL'S EQUATIONS

For purposes of elastic determinations it is usual to describe the structure
of these two substances with reference to ortho-hexagonal axes. The Z-axis
coincides with the trigonal axis and the X and Y-axes lie in a plane perpendi-
cular to the Z-axis   The X and Y-axes are chosen in such a manner that
the YZ-plane is a symmetry plane. The choice of reference axes is identical
with that employed by Voigt.

In obtaining differently oriented sections a clear and transparent natural
crystal of calcite showing the rhombohedral form was chosen. Its faces
were smooth and bright and the crystal as a whole was free from twinning.
Crystals of sodium nitrate were grown from solution and came out in the
usual rhombohedral forms. These crystals were grown a long time back
in connection with some magnetic studies. They are all well over five years
old and have been preserved in a desiccator. This was an advantage inasmuch
as it ensured a good seasoning of the crystals and placed them beyond the
period of plastic flow attendant upon freshly grown crystals. In both these
cases crystal plates cut perpendicular to the Z-axis (denoted by Z), perpendi-
cular to the X-axis (denoted by X), making 45° with Z and 45° with Y
(denoted by 45°) and making 135° with Z and 45° with Y (denoted by 135°)
have been cut and used. In obtaining these sections specially prepared
gadgets were used and the finest grade of abrasives have been employed.
Without going into the details of this technique it is sufficient if we say that
the orientations are correct to ± 30′ of arc.

Crystals belonging to this system have six independent constants as per
the scheme given below.

$$\begin{matrix} C_{11} & C_{12} & C_{13} & C_{14} & 0 & 0 \\ & C_{11} & C_{13} & -C_{14} & 0 & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & & & & C_{44} & 0 \\ & & & & & \frac{1}{2}(C_{11}-C_{12}) \end{matrix}$$

If we consider the propagation of sound in a direction l_s, m_s, n_s in a crystal of this class we have the following Christoffel's equations for the velocity of sound.

$$\begin{vmatrix} \lambda_{11} - \rho v^2 & \lambda_{12} & \lambda_{13} \\ \lambda_{12} & \lambda_{22} - \rho v^2 & \lambda_{23} \\ \lambda_{13} & \lambda_{23} & \lambda_{33} - \rho v^2 \end{vmatrix} = 0$$

where

$$\lambda_{11} = C_{11} l_s^2 + C_{66} m_s^2 + C_{44} n_s^2 + 2C_{14} m_s n_s$$
$$\lambda_{12} = 2C_{14} l_s n_s + (C_{66} + C_{12}) l_s m_s$$
$$\lambda_{13} = (C_{44} + C_{13}) n_s l_s + 2C_{14} l_s m_s$$
$$\lambda_{22} = C_{66} l_s^2 + C_{11} m_s^2 + C_{44} n_s^2 - 2C_{14} m_s n_s$$
$$\lambda_{23} = C_{14} l_s^2 - C_{14} m_s^2 + (C_{13} + C_{44}) m_s n_s$$
$$\lambda_{33} = C_{44} (l_s^2 + m_s^2) + C_{33} n_s^2$$

Solving these equations for the special cases we have

(a) For the Z cut plate

$$\rho v^2 = C_{33}; \quad \rho v^2 = C_{44}; \quad \rho v^2 = C_{44}.$$

All the modes are independent.

(b) For the X cut plate

$$\rho v^2 = C_{11}$$
$$\rho^2 v^4 - \rho v^2 (C_{44} + C_{66}) + C_{44} C_{66} - C_{14}^2 \, 0$$

The two coupled modes are the shear modes.

(c) For the 45° plate

$$\rho v^2 = \tfrac{1}{2} (C_{44} C_{66} \, 2C_{14})$$
$$\rho^2 v^4 - \rho v^2 \{ \tfrac{1}{2} (C_{11} + C_{33}) + C_{44} - C_{14} \} - \tfrac{1}{4} (C_{13} + C_{44} - C_{14})^2$$
$$+ \tfrac{1}{4} (C_{44} + C_{33}) (C_{11} + C_{44} - 2C_{14}) = 0.$$

The longitudinal and the shear modes are coupled in this case.

(d) For the 135° plate

$$\rho v^2 = \tfrac{1}{2} (C_{44} C_{66} - 2C_{14})$$
$$\rho^2 v^4 - \rho v^2 \{ \tfrac{1}{2} (C_{11} + C_{33}) + C_{44} + C_{14} \} - \tfrac{1}{4} (C_{13} + C_{44} + C_{14})^2$$
$$+ \tfrac{1}{4} (C_{44} + C_{33}) \, C_{11} + C_{44} + 2C_{14}) = 0.$$

Here again the longitudinal and the shear modes are coupled.

3. Experimental Determinations of the Elastic Constants

Measurements on calcite are given in Table I and those on sodium nitrate in Table II, along with other relevant data. In the case of 45° and

J. Bhimasenachar

135° plates the expressions entered in column 8 of the tables are the approximate solutions obtained by neglecting small coupling terms.

TABLE I

Measurements on Calcite

Plate No.	Section	Thick-ness in mks	Density	Transmis-sion fundamental in Mcs	Inten-sity	Mode	C'	
							Expression	Value
1	Z	1·93	2·704	1·407	s	L	C_{33}	7·98
1	Z	1·93	2·704	0·921	w	T	C_{44}	3·42
2	Z	2·85	2·704	0·956	s	L	C_{33}	8·03
2	Z	2·85	2·704	0·620	w	T	C_{44}	3·37
3	X	2·92	2·705	1·220	s	L	C_{11}	13·74
3	X	2·92	2·705	0·711	v w	T	$\frac{1}{2}(C_{11}-C_{13})$	4·068
3	X	2·92	2·705	0 613	w	T	C_{44}	3 47
4	45°	2·89	2·706	1·206	s	L	$\frac{1}{4}(C_{11}+C_{33}+4C_{44}+2C_{13} +4C_{14})$	13·14
5	135°	2·06	2·708	1·405	s	L	$\frac{1}{4}(C_{11}+C_{33}+4C_{44}+2C_{13} +4C_{14})$	9·074

TABLE II

Measurements on Sodium Nitrate

Plate No.	Section	Thick-ness in mm.	Density	Transmis-sion fundamental in Mcs.	Inten-sity	Mode	C'	
							Expression	Value
1	Z	1·790	2·270	1·133	s	L	C_{33}	3·74
1	Z	1·790	,,	0·853	w	T	C_{44}	2·12
2	X	2·495	,,	1·238	s	L	C_{11}	8·67
2	X	2·495	,,	0·614	w	T	C_{44}	2·13
2	X	2·495	,,	0 789	f	T	$\frac{1}{2}(C_{11}-C_{13})$	3·52
3	45°	1·970	,,	1·216	s	L	$\frac{1}{4}(C_{11}+C_{33}+4C_{44}+2C_{13} +4C_{14})$	5·21
4	135°	1·450	,,	1 894	s	L	$\frac{1}{4}(C_{11}+C_{33}+4C_{44}+2C_{13} +4C_{14})$	6·85

s—strong; w—weak; v w—very weak; f—faint, L—longitudinal, T—torsional.

In both the Tables, units for C' are 10^{11} dynes/cm ^{2}

Considering Table I and taking the measuremenmts of plates 1, 2 and 3 we have $C_{11} = 13·74$, $C_{33} = 8·01$, $C_{44} = 3·42$ as average values. Using the shear mode on the X-cut plate we have $C_{13} = 4·40$. Measurements on 45° and 135° plates are used to obtain C_{13} and C_{14} which come out as 4·50 and − 2·03 respectively. Thus the full set of the elastic constants of calcite are

$$C_{11} = 13·74,\ C_{33} = 8·01,\ C_{44} = 3·42,$$
$$C_{12} = 4·40,\ C_{13} = 4·50,\ C_{14} = -2·03\ \times 10^{11}\ \text{dynes/cm.}^2$$

Taking Table II and analysing in a similar manner we get the following elastic constants for sodium nitrate.

$$C_{11} = 8 \cdot 67, \quad C_{33} = 3 \cdot 74, \quad C_{44} = 2 \cdot 13,$$
$$C_{12} = 1 \cdot 63, \quad C_{13} = 1 \cdot 60, \quad C_{14} = 0 \cdot 82 \times 10^{11} \text{ dynes/cm.}^2$$

It is interesting to note here that C_{14} is negative for calcite while it is positive for sodium nitrate.

4. DISCUSSION OF RESULTS

We will first consider the results on calcite. It has already been stated that Voigt has made exhaustive measurements. Our values are compared with those of Voigt in Table III.

TABLE III

Elastic Constants of Calcite: Comparison against Values of Voigt

	C_{11}	C_{33}	C_{44}	C_{12}	C_{13}	C_{14}
Voigt ..	13·71	7·97	3·42	4·56	4·51	−2·08
Author ..	13·74	8·01	3·42	4·40	4·50	−2·03

There is complete agreement between the values of Voigt and our values.

Schæfer and Bergmann[12] have also studied this crystal by their optical method. But their numerical values have not been available to us for comparison.

Adams, Williamson and Johnston[1] have determined the compressibility of this substance and their value comes out as 13·9 when converted into the units employed here. The value of compressibility calculated from the relations given below comes out as 15·4. The agreement may be accepted though it is not very satisfactory.

$$\beta = (C_{11} + C_{13} + 2C_{33} - 4C_{13})/X$$
$$\beta_{\parallel} = (C_{11} + C_{13} - 2C_{13})/X$$
$$\beta_{\perp} = (C_{33} - C_{13})/X$$

where $X = (C_{11} + C_{12}) C_{33} - 2C^2_{13}$.

In the above expressions β is the volume compressibility, $\beta_{\parallel}$ and $\beta_{\perp}$ are the linear compressibilities parallel and perpendicular to the trigonal axis.

The ratio of the linear compressibilities comes out as 2·60 and compares very well with Bridgman's[13] determination of 2·68.

We now come to a consideration of the values of sodium nitrate. For comparison and check we have only Bridgman's[12] determinations of volume and linear compressibilities. These are compared against our values obtained by calculating with the help of the relations given above.

TABLE IV

Compressibilities of Sodium Nitrate

Compressibility		Bridgman	Author
β	..	3·85	3·40
$\beta_{\parallel}$	..	2·44	2·12
$\beta_{\perp}$	.	0·71	0·64

(Units are 10^{-13} cm.²/dyne)

In drawing conclusions from the above table it must be remembered that the values of the author are indirect evaluations while those of Bridgman are direct determinations. Further Bridgman has used a crystal grown from the melt while the author has used a crystal grown from solution and seasoned by preserving over several years. Considering these factors the agreement may be regarded as satisfactory.

Comparing the two substances between themselves we find that the elastic constants of sodium nitrate are generally lower than those of calcite which is in keeping with the lower hardness of $NaNO_3$ which is only 1·5 to 2·0 whereas that of $CaCO_3$ is 3·0.

5. REPRESENTATION OF THE ELASTICITY SURFACES

Surfaces of elasticity, one for the bending modulus and the other for the rigidity modulus, are drawn from the expressions for s'_{33} and $2 (s'_{44} + s'_{55})$ appropriate to this system of crystals and pertaining to a direction l_3, m_3, n_3. These expressions are given below:

$$s'_{33} = s_{11} (1 - n_3{}^2)^2 + s_{33} n_3{}^4 + (4s_{44} + 2s_{13}) (l - n_3{}^2) n_3{}^2 \\ + 4s_{14} m_3 n_3 (3l_3{}^2 - m_3{}^2)$$

$$2 (s'_{44} + s'_{55}) = 2 \{s_{44} + s_{66} + (s_{44} - s_{66}) n_3{}^2 + (s_{11} + s_{33} - 4s_{44} - 2s_{13}) (1 - n_3{}^2) n_3{}^2 \\ - 4s_{14} m_3 n_3 (3l_3{}^2 - m_3{}^2)\}$$

From these expressions we see that the sections of the surfaces by (001) are circular while those by (100) and (010) present some interesting features. Hence only the sections by these planes are drawn.

In order to be able to draw these sections the C's are converted into s's by using the formulæ given below.

$$(s_{11} + s_{12}) = C_{33}/X$$
$$s_{13} = -C_{13}/X$$
$$s_{33} = (C_{11} + C_{12})/X \qquad X = (C_{11} + C_{12}) C_{33} - 2C^2_{13}$$
$$2s_{14} = -2C_{14}/Y \qquad Y = 4(C_{44}C_{66} - C^2_{14})$$
$$4s_{44} = C_{66}/Z \qquad Z = C_{44}C_{66} - C^2_{14}$$
$$4s_{66} = C_{44}/Z$$

The values of the s's thus obtained in the two cases are tabulated in Table V.

TABLE V

Elastic Coefficients of CaCO$_3$ and NaNO$_3$

	s_{11}	s_{33}	$4s_{44}$	s_{12}	s_{13}	$2s_{14}$
CaCO$_3$ ..	11·0	17·3	39·4	−3·4	−4·3	8·6
NaNO$_3$ ..	13·4	30·8	51·5	−2·2	−4·8	−6·0

(Units are 10^{-13} cm.^{2}/dyne)

Figures 1 and 2 pertain to calcite and Figs. 3 and 4 to sodium nitrate.

50×10^{-13} cm.^{2}/dyne

$2(s'_{44} + s'_{66})$

s'_{33}

Fig. 1. Sections parallel to (100) of the Elasticity Surfaces of Calcite

J. Bhimasenachar
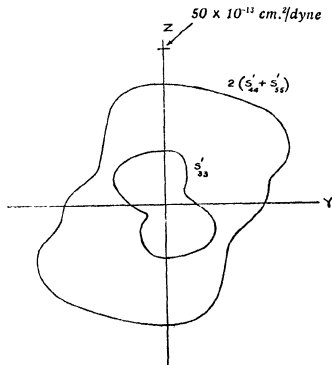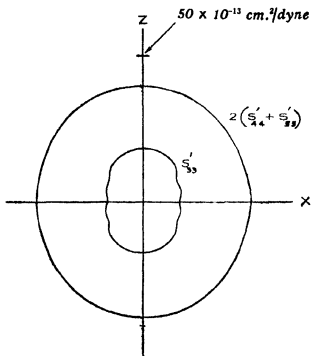
Fɪɢ. 2. Sections parallel to (010) of the Elasticity Surfaces of Calcite
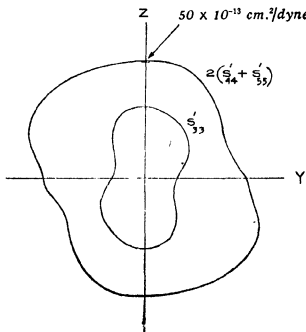
Fɪɢ. 3. Sections parallel to (100) of the Elasticity Surfaces of Sodium Nitrate
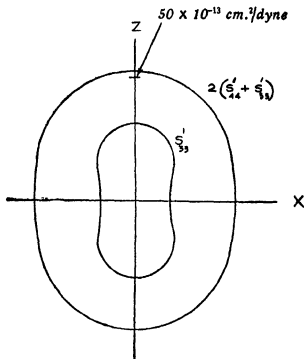
FIG. 4. Sections parallel to (010) of the Elasticity Surfaces of Sodium Nitrate

6. SUMMARY

Employing the new method developed by Bhagavantam and Bhima-senachar, the elastic constants of calcite and sodium nitrate are determined. The values on calcite fully support the existing data of Voigt. Determinations on sodium nitrate are made here for the first time. The values of the elastic constants for this crystal are:

$$C_{11} = 8 \cdot 67, \ C_{33} = 3 \cdot 74, \ C_{44} = 2 \cdot 13$$
$$C_{12} = 1 \cdot 63, \ C_{13} = 1 \cdot 60, \ C_{14} = 0 \cdot 82 \ \times 10^{11} \ \text{dynes/cm.}^2$$

J. Bhimasenachar

REFERENCES

1   .. Vide *International Critical Tables*.
2. Schæfer and Matossi   *Das Ultra Rote Spektrum*, 1930
3 Hibben   *The Raman Effect and Its Chemical Applications*, 1939.
   Bhagavantam   .   *Scattering of Light and the Raman Effect*, 1940.
4. Bragg   *Atomic Structure of Minerals*, 1937
5. Krishnan, Guha and   *Phil. Trans.*, 1933, **231**, 235
   Bannerjee
6. Chapman, Topping and   *Proc. Roy. Soc*, 1926, **111**, 25
   Morall
7 Lennard-Jones and Dent .   *Ibla.*, 1927, **113**, 690.
8 Topping and Chapman   .   *Ibid.*, 1927, **113**, 658.
9. Bhagavantam and Venkata-   *Proc Ind Acad Sci*, 1939, **9**, 224.
   rayudu
10. Sundara Rama Rao   ..   *Current Science*, 1944, **13**, 12 and *Proc. Ind. Acad. Sci.*, 1944,
                                    19, 93.
11 Voigt   .   *Lehrbuch der Kristallphysik*, 1928.
12. Bergmann   .   *Ultrasonics and Their Scientific and Technical Applications*,
                                    1938.
13 Bridgman   ..   *Proc. Amer Acad*, 1929, **64**, 51
   Wooster   ..   *A Text-Book on Crystal Physics*, 1938.

ELASTIC CONSTANTS OF APATITE

BY J. BHIMASENACHAR

(From the Department of Physics, Andhra University, Guntur)

1. INTRODUCTION

DURING the course of certain investigations relating to crystal elasticity in this Laboratory, it was realised that attention should be directed to the development of a new method which would permit us to handle small crystals and crystals occurring in nature and invariably showing mechanical defects such as cracks and crevices A suitable new method was developed and had been reported earlier.[1] It is now applied to the interesting case of apatite, a crystal belonging to the hexagonal system, and the results given in the present paper.

2. STRUCTURE OF APATITE

The crystals of apatite are generally simple combinations of prism and pyramid with or without the basal plane C. They are of various shades of blue, green, yellow or brown. They show a weak negative birefringence. The crystals have an imperfect cleavage parallel to the prism and the basal planes.

From the chemical point of view two sorts of apatite are to be distinguished: fluor-apatite and chlor-apatite. The first corresponds with the orthophosphate described by the formula Ca_4 (CaF) $(PO_4)_3$. In the second variety the fluorine is completely displaced by the chlorine to give the corresponding chlorine compound. There are also intermediate varieties containing both fluorine and chlorine, which are to be regarded as isomorphous mixtures of the pure compounds. Fluor-apatite is more common.

X-ray analysis[2] has shown that it can be best described by the space group C_{6A}^2. The unit cell contains two molecules. The crystallographic c is $6 \cdot 88$ A° while a is $9 \cdot 37$ A°.

Crystals used in these investigations are beautiful clear yellowish pieces about $2 \cdot 0$ to $2 \cdot 5$ cm. long and 6 to 8 mm. on the base. They were supplied by the Ward's Natural Science Establishment and said to have been obtained

209

from Durango, Mexico. The crystals presented the perfect, shining and planeprism faces. One end was terminated by the pyramidal faces.

3. Choice of Crystal Sections

This system of crystals has five independent elastic constants.

$$
\begin{array}{cccccc}
C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\
 & C_{11} & C_{13} & 0 & 0 & 0 \\
 & & C_{33} & 0 & 0 & 0 \\
 & & & C_{14} & 0 & 0 \\
 & & & & C_{14} & 0 \\
 & & & & & \frac{1}{2}\,(C_{11} - C_{12})
\end{array}
$$

To be able to calculate these constants one would have to make five independent measurements. The methods employed permit us to determine the longitudinal as well as the shear constants of a given crystal plate. On account of this fact three differently oriented sections would be sufficient to obtain the necessary data. But a few more plates are also examined and used as checks.

In cutting the necessary sections the crystal is referred to the ortho-hexagonal axes; the Z-axis coincides with the hexagonal axis and the equatorial plane contains the X and Y-axes, their positions being immaterial. Two Z-cut, one X-cut and one 45° cut sections are used for making the determinations. A section cut parallel to the pyramidal face is used as an internal check.

It has been pointed out in the earlier paper that the method requires a knowledge of the solutions of Christoffel's equations for the propagation of sound in crystalline media. Such solutions are included in Table I where experimental data are tabulated.

4. Determination of the Elastic Constants

The sections chosen above have been investigated thoroughly and the observations are tabulated in Table I along with other relevant data.

From the readings given in Table I we have $C_{11} = 16 \cdot 67$, $C_{33} = 13 \cdot 96$, $C_{44} = 6 \cdot 63$ as average values. Combining these with the longitudinal constant of the 45° plate we have $C_{13} = 6 \cdot 55$. Using the torsion constant

TABLE I

Measurements on Apatite

Plate No.	Section	Thickness in mm.	Density	Transmission fundamental f. in Mcs.	Intensity	Mode	C' Expression	Value
1	Z	0·53	3·218	6·245	v s	L.	C_{33}	14·10
1	Z	0·53	,,	4·200	s	T.	C_{44}	6·58
2	Z	0·91	,,	3·600	s	L.	C_{33}	13·81
2	Z	0·91	,,	2 505	w	T.	C_{44}	6 69
3	X	1·15	,,	3·130	s	L.	C_{11}	16·67
4	45°	1·73	,,	2·135	s	L.	¼ $(C_{11}+C_{33}+4C_4+2C_{13})$	17·56
4	45°	1·73	,,	1 363	w	T.	½ $(C_{44}+C_{66})$	7·157
5	Pyramid face	1·06	,,	3·483	s	L.	$C_{11}m_3{}^4+C_{33}n_3{}^4$ $+(4C_{44}+2C_{13})m_3{}^2n_3{}^2$	17·55

v s—very strong, s—strong, w—weak, L—longitudinal, T—torsional

Units of C' are 10^{-11} dynes/cm.$^{-2}$

of the same plate we obtain C_{13} as 1·31. Thus the complete set of elastic constants are

$$C_{11} = 16·67, \quad C_{33} = 13·96, \quad C_{44} = 6·63, \quad C_{13} = 6·55, \quad C_{12} = 1·31$$
$$\times 10^{11} \text{ dynes/cm.}^2$$

5. DISCUSSION OF RESULTS

In the first instance the internal consistency of the results is examined by considering the determination on the pyramidal face. In the expression for the effective longitudinal elastic constant of the plate l_3, m_3, n_3 are the direction cosines of the normal to the face and are given by $l_3 = 0$, $m_3 = \sin 40^\circ - 18'$ and $n_3 = \cos 40^\circ\text{-}18'$. Substituting these values in the expression we obtain the effective elastic constant as 17·28 whereas the observed value is 17·55. Considering the fact that in this case the longitudinal mode is a coupled mode and the solution given above is only an approximate one, the agreement may be regarded as very good.

A static torsion experiment was made on a plate with its length parallel to X-axis, breadth parallel to Y-axis and thickness parallel to Z-axis. The torsion constant for such a plate is given by C_{66}. As an average of three sets of static experiments C_{66} was obtained as 7·73 which compares very favourably with the dynamic value of 7·68.

The bulk modulus K of this material is calculated using the well-known relation

$$K = \frac{(C_{11} + C_{12})\,C_{33} - 2C_{13}{}^2}{C_{11} + C_{12} + 2C_{33} + 4C_{13}}$$

and comes out as $8 \cdot 39$. Bridgman's[3] determination of compressibility when converted into bulk modulus gives us a value of $9 \cdot 14$. The agreement may be regarded as satisfactory.

Auerbach[4] has determined the Young's modulus for the principal direction of a crystal of apatite and gives it as $13 \cdot 54$. This value does not check up with our determinations. The cause of the discrepancy is not known. It has not been considered as a serious objection in view of the fact that our determinations are self-consistent and agree well with the highly reliable compressibility determinations of Bridgman.

6. ELASTICITY SURFACES OF APATITE

Elastic properties of crystals are graphically represented by drawing two important surfaces.[5] One is the surface for the bending modulus and the other is the surface for the rigidity modulus. In the surface for bending modulus the radius vector is proportional to s'_{33} and in the surface for the rigidity modulus the radius vector is proportional to $2\,(s'_{44} + s'_{55})$.* It is usual to give sections of these surfaces by important crystallographic planes.

In order to be able to draw these surfaces the C's are converted into the s's using the following well-known relations.

$$(s_{11} + s_{12}) = C_{33}/X$$
$$s_{13} = - C_{13}/X$$
$$s_{33} = (C_{11} + C_{12})/X$$
$$4s_{44} = 1/C_{44}$$
$$4s_{66} = 1/C_{66}$$

where $X = C_{33}\,(C_{11} + C_{12}) - 2C^2{}_{13}$. The values of the s's are

$s_{11} = 6 \cdot 1$, $s_{33} = 10 \cdot 88$, $4s_{44} = 15 \cdot 08$, $s_{12} = 2 \cdot 36$, $s_{13} = - 3 \cdot 97 \times 10^{-13}$

cm. ^{2}/dyne.

---

* In the previous papers, in this paper and in the following papers the notation adopted in respect of the C's and the s's is that given by Wooster[6].

Expressions for s'_{33} and $2(s'_{44}+s'_{55})$ appropriate to the apatite class of crystals are

$$s'_{33} = s_{11}(1-n_3)^2 + s_{33}n_3^4 + (4s_{14}+2s_{13})(1-n_3^2)n_3^2$$

$$2(s'_{44}+s'_{55}) = 2\{s_{44}+s_{66}+(s_{44}-s_{66})\,n_3^2 + (s_{11}+s_{33}-4s_{44}-2s_{13})$$
$$\times(1-n_3^2)\,n_3^2\}$$

From these expressions it can be seen that sections by (100) and (010) planes are circular and the only interesting section is by (001). This section is shown in Fig. 1.
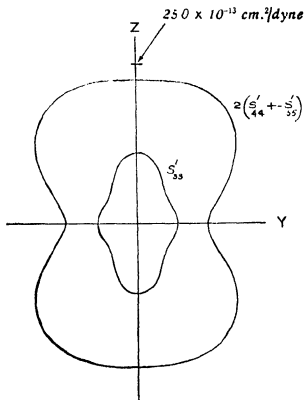

FIG 1. Sections parallel to (100) of the Elasticity Surfaces of Apatite

7. SUMMARY

Employing the new method developed by Bhagavantam and Bhima-senachar, the complete set of the elastic constants of apatite have been determined for the first time. The values are

$$C_{11}=16\cdot67,\ C_{33}=13\cdot96,\ C_{44}=6\cdot63,\ C_{13}=6\cdot55,\ C_{13}=1\cdot31$$
$$\times 10^{11}\ \text{dynes/cm.}^2$$

Surfaces for bending modulus and rigidity modulus are drawn and represented by their sections parallel to the hexagonal axis.

The author takes this opportunity of expressing his thanks to Prof. S. Bhagavantam, M.Sc., Hon. D.Sc., for his kind interest in the problem. The thanks of the author are also due to the authorities of the Andhra University for the award of the Raman Scholarship.

REFERENCES

1.	Bhagavantam and Bhima-senachar	*Proc. Ind Acad Sci*, 1944, 20, 298.
2.	Bragg	*Atomic Structure of Minerals*, 1937
3.	Bridgman	*Sill Journ*, 1928, 13, 287
4	Auerbach	Vide *Landolt-Bornstein Tabellen, HwI*
5.	Wocster	*A Text-Book on Crystal Physics*, 1938.

CONSTITUTION OF PATULETIN—PART I

BY L. RAMACHANDRA ROW AND T. R. SESHADRI

(From the Department of Chemistry, Andhra University)

Received September 12, 1945

It has been shown in previous papers[1] that patuletin[a] is not identical either
with 5 : 6 : 3′ : 4′-tetra-hydroxy-flavonol or with the 6 : 7 : 3′ : 4′-isomer as was
originally considered probable. Consequently the compound has been
reinvestigated, particular attention being paid to the identification of the
products of fission.

For this purpose patuletin had to be methylated Since during the
period of this work, methylating agents such as methyl iodide and dimethyl
sulphate were not available in the market due to the conditions of war and
had to be prepared for use, attempts were made to effect strict economy
in the reagent. As methyl iodide is volatile and losses are heavy, it was
unsuitable. Further it does not invariably bring about complete methyla-
tion. The method of methylation adopted by Rao and Seshadri[2] using the
acetyl derivative of the pigment had to be given up in view of the large
quantities of dimethyl sulphate required. However, methylation with
dimethyl sulphate and anhydrous potassium carbonate in anhydrous acetone
medium was found to be quite suitable. Dimethyl sulphate being non-
volatile, losses of the methylating agent are negligible. Further acetone is
an excellent medium for methylating hydroxy-flavones and flavonols In
this process even the resistant 5-hydroxyl group gets methylated readily and
yields are uniformly satisfactory.

When patuletin was methylated in this way, a colourless crystalline
product melting at 141–42° (I) was obtained. It was insoluble in aqueous
alkali, cold or warm, and gave no ferric chloride colour. However, this
product was not identical with the ether (II) obtained previously by Rao
and Seshadri.[2] The new product depressed the melting point of the older
one. On closer examination, it was discovered that the latter was only
a partially methylated derivative of patuletin. Though insoluble in the
cold, it was soluble in warm aqueous alkali and gave a brown colour
with neutral alcoholic ferric chloride. These reactions are characteristic of
a free 5-hydroxyl. A repetition of the older method of methylation using
patuletin acetate yielded the same product (II) giving all the reactions for

a free 5-hydroxyl. It is extraordinary and difficult to explain the formation of this partially methylated product in view of the fact that the method yielded completely methylated derivatives in the case of quercetagetin, herbacetin, quercetin, cannabiscetin and gossypetin acetates.[3] However, the formation of methyl ether (II) established the presence of a 5-hydroxyl group in patuletin.

When subjected to fission with 50% aqueous potash, the completely methylated derivative of patuletin (I) yielded an acid which was identified to be veratric acid (III) both by analysis and by direct comparison with an authentic sample. An ortho-hydroxy-ketone (IV) was also isolated as another product of degradation and it had the formula $C_{12}H_{16}O_6$. Estimation of methoxyls gave evidence for four methoxyls in the ketone. It was, therefore, considered to be a tetra-methoxy-ortho-hydroxy-acetophenone. From the composition of fission products, it could be inferred that the new methyl ether of patuletin (I) should be a hexamethyl ether. This was supported by analysis both for methoxyls and carbon and hydrogen. Rao and Seshadri's compound (II) has now been shown to be a pentamethyl ether with a free hydroxyl still left. On further methylation using dimethyl sulphate and aqueous alkali in acetone medium at 60° it yielded a product identical with the new methyl ether (I).

The formation of hexa- and penta-methyl ethers necessitated a closer and more detailed analytical study of patuletin. Careful Micro-Zeisel estimation showed the presence of one methoxyl. This important fact was somehow missed by the previous workers and the matter escaped careful check probably because the analytical values for C and H agreed closely with the requirements of a penta-hydroxy-flavonol. Patuletin has now, therefore, been assigned the elementary formula $C_{16}H_{12}O_8$ instead of the previous formula $C_{15}H_{10}O_7$. The new formula is in greater accord with the analytical results for patuletin and its acetate. It is a monomethyl ether of a flavonol having six hydroxyl groups. The isolation of veratric acid and a tetramethoxy-ortho-hydroxy-acetophenone (IV) as the degradation products of the methyl ether (I) proves that two of the six hydroxyls are situated in the side-phenyl nucleus and the remainder in the benzo-pyrone part.

Of the naturally occurring flavonols containing six hydroxyl groups only quercetagetin and gossypetin possess two hydroxyl groups in the side-phenyl nucleus. A close resemblance between the former and patuletin has already been noted by previous workers. The following table gives the comparative data between patuletin and quercetagetin:
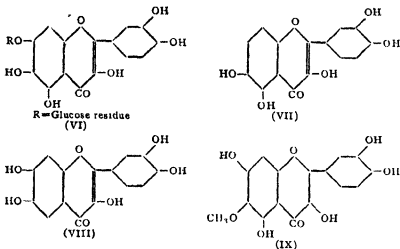
	Patuletin	Quercetagetin
1. Molecular formula	$C_{16}H_{12}O_8$	$C_{15}H_{10}O_8$
2. Melting point	261–62°	315–18°
3. Acetate, m.p.	171–72°	209–10°
4. Methyl ethers	(a) Partially methylated compound, m.p. 159–60°	(a) Penta-methyl ether, m.p 159–60°
	(b) Completely methylated compound, m.p. 141–42°	(b) Hexamethyl ether, m p. 141–42°

Authentic samples of penta- and hexa-methyl ethers of quercetagetin were obtained from quercetagetin isolated from the flowers of *Tagetes erecta*, and mixed melting points with the partially methylated (II) and completely methylated (I) derivatives of patuletin were determined In both cases there was no depression. It was thus conclusively proved that patuletin is a monomethyl ether of quercetagetin. The identification was complete when quercetagetin (V) was obtained on demethylating patuletin with hydriodic acid.

PATULETIN

It therefore follows that the ketonic fission product (IV) is quercetagetol tetramethyl ether. This has been obtained pure for the first time now; the yield is good if absolute alcoholic potash is employed for the fission and water is avoided. The corresponding tetra-ethyl compound was prepared by Perkin[4] by the alkaline degradation of quercetagetin hexa-ethyl ether. Nelson and Goldsworthy and Robinson[5] in connection with their work on tangeretin characterised the methyl ether as its oxime. The ketonic compound (IV) now obtained, yields an oxime having the properties described by them.

The position of the methoxyl in patuletin was next investigated. A comparative study of the colour reactions of patuletin and quercetagetin in alkaline buffer solutions showed marked differences. Quercetagetin developed a greenish yellow colour initially which changed over to green during the course of an hour. Within 24 hours, the solution became brownish yellow. Except for the increase in intensity and rapidity of the colour change, the sequence of colours was almost the same throughout the range of pH (8·6 to 13·4) employed. Patuletin did not exhibit such a marked change in colour. The initial colour was bright yellow in all cases and showed little or no change during the course of an hour. After 24 hours the colours ranged from orange to orange-brown and pink. Since these colour reactions are primarily controlled by the composition of the benzo-pyrone part, it was considered probable that the marked differences between quercetagetin and patuletin is caused by the presence of the methoxyl in this part of the molecule. The ease with which patuletin could be oxidised in alkaline solution by means of atmospheric oxygen suggests that the 3-hydroxyl is free and not methylated. The formation of the penta-methyl ether further excludes the 5-hydroxyl. Hence the position of the methoxyl should be either 6 or 7.

A comparison has again been made of the colour reactions of patuletin with those of (1) quercetagitrin (VI) having the glucose unit attached to the hydroxyl in the 7-position, (2) 3:5:6:3′: 4′-penta-hydroxy-flavone (VII) in which there is no hydroxyl in the 7-position and (3) 3:6:7:3′: 4′-penta-hydroxy-flavone (VIII) having no hydroxyl in the 5-position. The difference is definite. There is marked change of colour from the initial yellow within an hour in the most in these three cases whereas patuletin resembles quercetin (a 5:7-dihydroxy compound) in giving a yellow colour stable for several hours. It may therefore be suggested tentatively that patuletin has the methoxyl in the 6-position (IX).

OH
O
RO—
HO—
—OH
OH
CO
—OH
OH
R = Glucose residue
(VI)

OH
O
HO—
—OH
CO
OH
—OH
(VII)

OH
O
HO—
—OH
CO
HO—
—OH
(VIII)

OH
O
HO—
—OH
CH₃O—
CO
OH
OH
(IX)

EXPERIMENTAL

Methylation of Patuletin:

(a) *Hexa-methyl ether* (I).—A solution of dry patuletin (1·0 g.) in anhydrous acetone (150 c.c.) was treated with dimethyl sulphate (2·0 c.c.) and freshly ignited potassium carbonate (15 g.) The mixture was refluxed on a water-bath for 30 hours. At intervals of eight hours, further quantities (2·0 c.c.) of dimethyl sulphate were added to the refluxing liquid. A total of 8 c.c. of the reagent was thus used. After 30 hours, the acetone solution was filtered and the potassium salts washed with three lots of warm acetone (30 c.c.). The filtrate was concentrated on a water-bath and to the concentrate, water (50 c.c.) was added when fine colourless needles of the methyl ether separated out. The potassium salts were dissolved in water and the solution acidified with hydrochloric acid. There was no appreciable precipitate. The crystalline methyl ether was re-crystallised twice from alcohol when it was obtained as shining colourless prismatic needles melting at 141–42°. Yield: 0·65 g. (Found: C, 62·6; H, 5·4; OCH₃, 45·9; C₂₁H₂₂O₈ requires C, 62·7; H, 5·5; and OCH₃, 46·3%.) The methyl ether was insoluble in cold or warm aqueous sodium hydroxide. It gave no colour with neutral ferric chloride in alcoholic solution. It depressed the melting point of the methyl ether obtained by Rao and Seshadri.[a]

(b) *Penta-methyl ether* (II).—The methyl ether obtained by Rao and Seshadri[a] was crystallised twice from alcohol. It came out as very pale yellow needles melting at 159–60°. Even when a third crystallisation was carried out using some animal charcoal, the compound retained a yellow tinge. It was insoluble in cold aqueous sodium hydroxide but dissolved

when warmed yielding a bright yellow solution. With ferric chloride, it
developed a brown colour in alcoholic solution. These reactions are
characteristic of a free 5-hydroxyl in the compound.   To verify if the
same partially methylated compound would again be obtained, patuletin
was acetylated and methylation carried out according to the method of
Rao and Seshadri.[2]

Acetyl patuletin (0·5 g.) was methylated in acetone medium by means
of dimethyl sulphate (20 c.c.) and aqueous sodium hydroxide (20%, 40 c.c.).
The reagents were added alternately in three lots with vigorous stirring
and cooling under the tap. The methyl ether was obtained as very pale
yellow shining needles melting at 159–60° and was identical with the older
sample; the mixed melting point was not depressed. (Found: C, 61·9
H, 4·8; OCH$_3$, 40·1; C$_{20}$H$_{20}$O$_8$ requires C, 61·9; H, 5·2; and OCH$_3$,
40·0%. Rao and Seshadri recorded OCH$_3$, 39·6%.)

The above experiment was repeated with the following modifications
(cf. Anderson) to find out if a completely methylated compound could be
obtained.

(1) Dimethyl sulphate (20 c.c.) was added to the acetone solution of
the patuletin acetate in one lot and then the alkali (20%, 40 c.c.) in small
lots. Cooling was employed when the mixture became hot in order to save
the solvent and to moderate the speed of the reaction.

(2) Same as (1) above except that the mixture was not cooled under
the tap and the loss of acetone due to the high temperature attained during
the course of the reaction was made good by adding more of acetone.

The product in both cases was again the partial methyl ether. In
these experiments, the yields were frequently low and the product required
careful purification.

Methylation of Penta-methyl ether (II).

The penta-methyl ether (0·1 g.) was dissolved in acetone (20 c.c.) and
treated with aqueous sodium hydroxide (10 c.c.) and dimethyl sulphate
(2 c.c.) in small quantities alternately, keeping the solution at 60°   Through-
out the addition the solution was kept stirred. The pale yellow liquid was
left in the water-bath at 60° for an hour more and the acetone was distilled
off. The residual solution was then acidified with hydrochloric acid and
left in the ice-chest for a number of hours when the completely methylated
compound separated. It crystallised from aqueous alcohol (animal charcoal)
in the form of white prismatic needles melting at 141–42°. It did not
depress the melting point of the hexa-methyl ether (I).

Alkaline Oxidation of Patuletin

Degradation of patuletin in 50% aqueous potash was repeated following the general procedure given by Rao and Seshadri.[3] The products of oxidation were methylated with dimethyl sulphate in the usual manner. The liquid was acidified and extracted with ether. The ethereal extract was washed with water and then with aqueous sodium bicarbonate On acidifying the sodium bicarbonate layer, a colourless crystalline solid was obtained. It crystallised from hot water in the form of colourless rhombic needles melting at 181–82°. It was identified as veratric acid since it did not depress the melting point of an authentic sample

Alkaline Hydrolysis of the Hexa-methyl ether (I)

(*a*) The methyl ether (1·5 g.) was refluxed in a silver flask with 50% aqueous potash (30 c.c.) for eight hours, the heating being effected in an oil-bath kept at 150–55°. After cooling the flask, the contents were transferred to a conical flask, and acidified with hydrochloric acid A pale yellow solid separated out. It was thoroughly macerated with sodium bicarbonate solution (10%) and filtered.

Veratric acid.—On acidifying the bicarbonate filtrate, a white crystalline solid separated out. It was crystallised twice from hot water using a small quantity of animal charcoal. It was obtained in the form of colourless rhombic needles radiating from a point. It was identical with veratric acid and did not depress the melting point of an authentic sample. Yield: 0·3 g. (Found: C, 59 3; H, 5·2; OCH₃, 34·6; $C_9H_{10}O_4$ requires C, 59·3; H, 5·5; and OCH₃, 34·1%.)

Ketonic compound (IV): Quercetagetol-tetra-methyl ether.—The residue which was insoluble in sodium bicarbonate was washed well with water and then crystallised from hot water. It was obtained in the form of colourless narrow rectangular plates melting at 75–76°. Yield: 0 2 g. (Found: C, 56·5; H, 6·2; OCH₃, 48·0; $C_{13}H_{16}O_6$ requires C, 56 3; H, 6·3; and OCH₃, 48·4%.) It was very easily soluble in cold aqueous sodium hydroxide forming a pale yellow solution. With ferric chloride, it gave a brown colour in alcoholic solution.

(*b*) The hydrolysis of the hexa-methyl ether (1 g.) was also carried out using absolute alcoholic potash (7%, 30 c.c.). The mixture was refluxed for six hours over a water-bath. After removing the alcohol by evaporation, the residue was dissolved in water (30 c.c.) and acidified with hydrochloric acid. The mixture was extracted five times with ether and the ethereal extract shaken thrice with sodium bicarbonate to remove the acid component.

On acidifying the bicarbonate extract, the acid was obtained in a colourless crystalline condition. It was identical with veratric acid. Yield: 0·3 g. The ether layer was then washed with a little water and evaporated to dryness. On vigorous stirring, the residue solidified into a pale yellow crystalline mass. When crystallised from water, it was obtained as colourless narrow rectangular plates melting at 75–76°. It was identical with the ketone obtained in the earlier experiment; yield: 0·6 g.

Demethylation of Patuletin: Formation of Quercetagetin.—A cold solution of patuletin (0·5 g.) in acetic anhydride (3 c.c.) was treated with hydriodic acid (d. 1·7, 10 c.c.) slowly with shaking and cooling under the tap. The mixture was refluxed, in an oil-bath at 150–55° for three hours and then poured into about 50 c.c. of water. The solution was then decolourised by passing sulphur dioxide when a pale yellow compound settled down. It was filtered and crystallised from aqueous alcohol. It was obtained in the form of short needles and plates melting at 315–18° and was found to be identical with quercetagetin. (Found in air-dried sample: C, 50·6; H, 4·0; $C_{15}H_{10}O_{8},2H_2O$ requires C, 50·9 and H, 4·0%.)

A part of this substance was acetylated by refluxing with acetic anhydride and anhydrous sodium acetate. When the product was crystallised from acetic acid using a little animal charcoal, the acetyl derivative was obtained as long rectangular plates melting at 209–10°. It did not depress the melting point of an authentic sample of acetyl quercetagetin.

Patuletin and Patuletin-penta-acetate.—For purposes of analysis, patuletin was crystallised twice from alcohol when it was obtained as yellow needles melting at 261–62° as already recorded. A third crystallisation was also made but it did not improve the melting point. (Found in air-dried sample: C, 52·6; H, 4·4; OCH_3, 8·4; $C_{16}H_{12}O_8$, 2H_2O requires C, 52·2; H, 4·4; and OCH_3, 8·4%. Found in the sample dried at 110–20° *in vacuo*: C, 57·7; H, 3·6; $C_{16}H_{12}O_8$ requires C, 57·8 and H, 3·6%.) The penta-acetate crystallised from dilute acetic acid in the form of colourless needles melting at 171–72°. (Found: C, 57·9; H, 4·4; $C_{26}H_{22}O_{13}$ requires C, 57·6; H, 4·1%. Rao and Seshadri found C, 58·1; H, 3·9%.)

Colour Reactions in Buffer Solutions

The following buffer solutions prepared from the "Universal Buffer Mixture" (B.D.H.) were employed for studying the colour reactions of the flavonols: (1) pH 8·6; (2) pH 9·8; (3) pH 11·0; (4) pH 12·2; and (5) pH 13·4.

Patuletin.—(1–3) Yellow solution undergoing no change in an hour. After 24 hours the colours ranged from orange to brighter orange with a tinge of pink. (4) Stronger yellow with no change in an hour; after 24 hours dull orange with a tinge of pink. (5) The initial yellow colour changed to brown in the course of 30 minutes; after 24 hours brownish yellow.

3 : 5 : 6 : 3′ : 4′-*Penta-hydroxy-flavone.*—(1) and (2) Deep yellow rapidly turning brown; after an hour deep brownish yellow; after 24 hours to pale brown. (3) Brighter yellow; within two minutes reddish brown, stable even after an hour; after 24 hours almost colourless. (4) Bright yellow changing to reddish brown and finally pink within two minutes; after an hour fading; after 24 hours colourless solution. (5) Immediately reddish brown rapidly turning pink; after an hour fading; after 24 hours colourless solution.

3 : 6 : 7 : 3′ : 4′-*Penta-hydroxy-flavone.*—(1) Feeble yellowish green fairly stable; after 24 hours pinkish yellow. (2) and (3) Yellowish green becoming more intense; after 24 hours pinkish orange. (4) Yellow slowly turning brown; after half-an-hour brownish yellow; after 24 hours bright orange. (5) Yellow turning brown rapidly; after an hour brownish yellow; after 24 hours pale brown.

The colour reactions of quercetagetin and quercetagitrin were as already reported.[6]

Bargellini's Test

The test was carried out by treating a solution of the flavonol (3–5 mg.) in absolute alcohol (10 c.c.) with 3% sodium amalgam and noting the changes. The following hydroxy-flavonols were tested.

(1) *Quercetagetin.*—There was immediate separation of green flocks. When left overnight, they turned brown.

(2) *Quercetagitrin.*—Rapid separation of brown flocks. On the following day, they appeared greenish brown.

(3) *Patuletin.*—Just as in quercetagetin, there was rapid formation of green flocks. After 24 hours, they became yellowish brown.

(4) 3 : 5 : 6 : 3′ : 4′-*Penta-hydroxy-flavone.*—Brown flocks as in quercetagitrin. They turned yellowish brown on keeping overnight.

(5) 3 : 6 : 7 : 3′ : 4′-*Penta-hydroxy-flavone.*—The solution turned bright green only. There was no separation of flocks. Next morning there was only a trace of brown precipitate but no flocks.

(6) *Quercetin.*—Immediately the solution turned yellow with **no flocks**. The colour slowly changed to brown.

SUMMARY

The methylation of patuletin has been reinvestigated. It forms two methyl ethers, one with five methoxyl groups and the other with six. Decomposition of the latter with alcoholic alkali yields quercetagetol-tetra-methyl ether and veratric acid. Demethylation of patuletin produces quercetagetin. Patuletin is shown to be a mono-methyl ether of quercetagetin; from a study of its properties and reactions and from a comparison with related compounds, the methoxyl is tentatively considered to be in the 6-position.

REFERENCES

1	Row and Seshadri	.. *Proc. Ind. Acad. Sci.*, 1944, **21**, 130 and 155.
2	Rao and Seshadri	.. *Ibid.*, 1941, **14**, 643
3	————	.. *Ibid.*, 1939, **9**, 177 ; *Curr. Sci.*, 1939, **8**, 255.
4.	Perkin	*J. C. S. Trans.*, 1913, **103**, 209
5.	Nelson	. *J. Amer. Chem. Soc.*, 1934, **56**, 1392.
6.	Goldsworthy and Robinson	*J. C. S.*, 1937, 47.
7.	Anderson	. *Canad. J. Res.*, 1932, **7**, 285.
8.	Rao and Seshadri	.. *Proc. Ind. Acad. Sci.*, 1941, **14**, 293

INHIBITION OF THE *LIGHT-EFFECT* BY RESISTIVE IMPEDANCE IN ELECTRIC DISCHARGE

By S. S. JOSHI

(From the Department of Chemistry, Benares Hindu University)

ARISING out of work on the production of a new *light-effect*,[1,2,3] namely, the *decrease* on irradiation of the current in a gas especially chlorine under electrical discharge, was the observation that the net *light-effect* $\triangle i$ as well as $\% \triangle i$ that expressed as a percentage of the discharge current i through chlorine in a sealed ozoniser apparently varied with the nature of the A.C. indicator employed.[1,2,3] This was investigated in some detail, using the Cambridge vacuo-junctions of various heater resistances which carry i.

These vacuo-junctions have a low capacity and inductance; a stable characteristic over a wide range of applied potential V, and frequency of the A.C. supply n; and are markedly sensitive to current change since the galvanometer deflexions are proportional to i^2. Using different vacuo-junctions, results for the *light-effect* agreed within 2 per cent. for approximately equal heater resistances. Increase of the last from 25 to 1,800 ohms *decreased* the corresponding $\% \triangle i$. This agrees with a general result I have observed, that whilst the introduction of an external stabilising resistance rendered i steady, the corresponding $\% \triangle i$ was smaller. This influence of an external resistance on the magnitude of the *light-effect* is illustrated by the following results which are typical of a series of observations. The P.D. across a 5,000-ohm resistance R introduced between the low tension electrode and earth was observed with a Ferranti electrostatic and also thermionic valve voltmeter; the percentage *light-effect* $\% \triangle i$ using the latter for example at 4 kV and 50 cycles frequency was 11; it increased to 29, when R was substituted by a low resistance vacuo-junction. This disparity obtained over a wide range of V the applied potential; it also increased by increasing R at constant V.

The ozoniser was next earthed through R and a vacuo-junction in series. At 6·7 kV increase of R from 0 to 500,000 ohms, diminished the corresponding current i from 7·1 to 6·9 in arbitrary units, the effect being comparatively pronounced at small R. This could not be attributed to a by-passing of the high frequencies in i through the stray capacity

225

between ozoniser and the earth, since i_{aerial} the corresponding current picked up by a frame aerial about 4 ft. from the ozoniser, *decreased* from 2·74 to 2. This influence of R was observed with ozonisers filled with different gases; excited at various V; by transformers of widely different capacities; and also under such conditions of discharge which produced a negligibly small *light-effect*. Furthermore, a Kelvin-White electrostatic voltmeter connected directly across the ozoniser terminals showed but an inappreciable diminution of the corresponding V, on introducing R up to 500,000 ohms between the L.T. terminal and earth. This was not due to insensitivity of the voltmeter, since V had to be increased markedly to restore i with R to that without it

The above observations applied also to the *light-effect*. Irradiation did not alter V corresponding to $\triangle i$. It is also significant that this decrease of i by R tends to a maximum near the 'threshold potential' V_m, [4, 6, 7 8] where % $\triangle i$ is comparatively pronounced

Evidence was adduced previously showing that the *light-effect* is caused by a decrease of the amplitudes of especially the high frequency components of i. That R acts likewise, that is, mainly damps the H.F., appeared from oscillograms of i under various R; this follows also from general considerations of an oscillatory discharge of a condenser (such as an ozoniser) in a resistive circuit The preferential damping of the H.F. by R explains the observed reduction in the corresponding aerial current i_{aerial} which is predominantly H F. Thus, for example at 6·7 kV, i_{aerial} diminishes from, 2·74 to 2 due to R. Compared with this effect of R on i cited earlier, that on % $\triangle i$ is generally much larger. At 6·7 kV, for example, without and with R, % $\triangle i$ was 25 and 2 respectively. The H.F. represents therefore, but a limited proportion of i. *That, however, the light-effect is more than an analogue of* R *is suggested by a general result that, whilst* 1, % $\triangle i$ *in* i, *and* i_{aerial} *decrease under* R, *the corresponding percentage light-effect in* i_{aerial} *increases*; this was, for example, 22 without R and 36 with R at 6·7 kV.

It was observed subsequently that the wattage dissipated in the ozoniser, which is negligibly small below V_m, the 'threshold potential' *decreases* corresponding to $\triangle i$ The *light-effect* entails therefore, a reduction of the conductance or ohmic part of i. That the corresponding displacement current may also be affected is suggested by a frequent observation of a sensible movement and distortion on irradiation of the steadied wave-form on the oscillograph, due perhaps to a frequency or/and phase shift; by the observed influence on % $\triangle i$ of capacitative changes in the system, suggesting a change under light of the dielectric constant of the ionised gas

as a possibly partial, though at best a minor explanation of this pheno-
menon; of ' aging ', adsorption and the nature of the wall material.

Metallic and other type films deposited on the annular walls alter
appreciably both i and % Δi; in this, secondary emission of ions from these
surfaces is possibly an important factor. From results of an investigation
of over 50 substances studied by Cherian in these Laboratories over a
wide range of conditions, it appears that with metallic films and those of
stable substances such as alkali chlorides, i increases but %Δi diminishes.
Some of these results revealed a remarkable alteration in Δi and % Δi,
and under certain repeatedly observed but hitherto insufficiently reproducible
conditions, a *positive light-effect* using chlorident detectors. Plausible on
familiar theories of the classical photo-electric and allied effects, such a
current gain under light and its comparative rarity under general condi-
tions productive of the *light-effect*, have an obvious significance for a
mechanism of this phenomenon.

SUMMARY

An ohmic resistance R introduced between earth and the low tension
electrode of a Siemens' tube decreases markedly the discharge current i;
it does not, however, affect the corresponding potential V determined
electrostatically across the ozoniser. R decreases markedly the percentage
light-effect in i; this is attributed partly to a preferential damping of the
high frequency components of i which are found by the author to be the
chief seat of this phenomenon.

REFERENCES

1	Joshi	*Pres Address, Chem Sec. Ind Sci Cong.*, 1943
2	———	*Curr Sci.*, 1945, 14, 67
3.	———	*Benares Hindu University J.*, 1943, **8**, 99.
4.	———	*Nature*, 1944, **154**, 147
5.	———	*Curr. Sci*, 1944, **13**, 253
6	——— and Lad	*Proc Ind Sci Cong , Chem Sec , Abst ,* 1945
7	Joshi	*Curr Sci ,* 1939, **8**, 548
8.	———	*Trans Farad Soc ,* 1927, **23**, 227 ; 1929, **25**, 108, 138
9.	Cherian	*Proc Ind Sci Cong , Chem Sec ,* 1945
10	Joshi	*Curr Sci ,* 1945, **14**, 35 ; 1944, **13**, 278
11	Parshad	*Nature*, 1945, **155**, 362

SOME NEW KERNELS FOR THE DERIVATION OF SELF-RECIPROCAL FUNCTIONS

By H. C. GUPTA, PH.D.

(Christ Church College, Cawnpore)

§ 1. INTRODUCTION

FOLLOWING Hardy and Titchmarsh we shall call a function R_ν if it is self-reciprocal in the Hankel transform of order ν, that is, if it satisfies the integral equation

$$f(x) = \int_0^\infty \sqrt{xy}\, J_\nu(xy) f(y)\, dy, \qquad R(\nu) > -1. \qquad (1 \cdot 1)$$

A number of rules for the derivation, from a known R_μ function, of another self-reciprocal function of a different order, ν, say, has been given from time to time by several authors.* One such rule is that if $f(x)$ is R_μ, then the function

$$g(x) = \int_0^\infty P(xy) f(y)\, dy \qquad (1 \cdot 2)$$

is R_ν provided that

$$P(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} 2^s\, \Gamma\left(\tfrac{1}{4} + \tfrac{1}{2}\mu + \tfrac{1}{2}s\right)\, \Gamma\left(\tfrac{1}{2}\nu + \tfrac{1}{4} + \tfrac{1}{2}s\right) F(s)\, x^{-s}\, ds, \qquad (1 \cdot 3)$$

where $F(s) \equiv F(1 - s)$.

The symmetry in μ and ν of the integrand of $(1 \cdot 3)$ shows that if $f(x)$ is R_ν, then $g(x)$ is R_μ. The function $P(x)$ is called a kernel for transforming an R_μ into an R_ν and vice versa. We shall indicate this by saying that the kernel is $C(\mu, \nu)$.

In the present paper a few kernels have been investigated by this rule and employed to derive some new R_ν functions.

---

* E C. Titchmarsh, *Theory of Fourier Integrals* (Oxford, 1937), § 9·14. Besides the references given there on p 267, see W. N Bailey, *Jour. London Math. Soc.*, 1931, **6**, 242–47 and B Mohan, *Proc. Physico-Math. Soc Japan*, 1936, **18** (3), 133–34 ; *Quart. Jour. of Ma.h*, 1939, **10**, (40), 252–60, *Indian Jour. of Physics*, 1941, **15**.

2. Three Kernels of the Type $x^\lambda I_n (\tfrac{1}{2}x) K_m (\tfrac{1}{2}x)$

The limiting case of MacRobert's integral‡ may be put in the form

$$\int_0^\infty x^{s-1}x^\lambda\, I_n (\tfrac{1}{2}x)\, K_m (\tfrac{1}{2}x)\, dx =$$

$$\frac{\Gamma\{\tfrac{1}{2}(1-\lambda-s)\}\,\Gamma(1-\tfrac{1}{2}\lambda-\tfrac{1}{2}s)\,\Gamma_2\{\tfrac{1}{2}(n+\lambda\pm m+s)\}}{\sqrt\pi\; 2^{5-\lambda-s}\,\Gamma_2\{\tfrac{1}{2}(n-\lambda-s\pm m)+1\}},$$

where $R(-n\pm m)<R(\lambda+s)<1$. Since the integral is absolutely convergent, it follows by Mellin's Inversion Theorem§ that

$$x^\lambda\, I_n (\tfrac{1}{2}x)\, K_m (\tfrac{1}{2}x) = \frac{1}{2\pi i}\int_{s-i\infty}^{s+i\infty} (\tfrac{1}{2}x)^{-s}\,\Gamma(\tfrac{1}{2}\nu+\tfrac{1}{4}+\tfrac{1}{2}s)\,\Gamma(\tfrac{1}{2}\mu+\tfrac{1}{4}+\tfrac{1}{2}s)\,F(s)\,ds, \quad (2\cdot1)$$

where

$$F(s) = \frac{\Gamma\{\tfrac{1}{2}(1-\lambda-s)\}\,\Gamma\{1-\tfrac{1}{2}\lambda-\tfrac{1}{2}s\}\,\Gamma_2\{\tfrac{1}{2}(\lambda+n\pm m+s)\}\,2^{\lambda-s}}{\Gamma_2\{\tfrac{1}{2}(n-\lambda\pm m-s)+1\}\,\Gamma\{\tfrac{1}{2}(\nu+s+\tfrac{1}{2})\}\,\Gamma\{\tfrac{1}{2}(\mu+s+\tfrac{1}{2})\}\,\sqrt\pi}$$

On comparing with (1 3) we find that the function on the left of $(2\cdot1)$ is a kernel if $F(s)\equiv F(1-s)$, which requires that the parameters

$$-\tfrac{1}{2}-\lambda,\ \tfrac{1}{2}-\lambda,\ \nu,\ \mu = n\pm m\pm(\tfrac{1}{2}-\lambda)$$

$3n+\tfrac{1}{2}$, $-n-\tfrac{1}{2}$ severally but in any order. This admits of three valid solutions:

(i) $m=n=-\lambda$; $\mu=\tfrac{1}{2}+3n$, $\nu=-n-\tfrac{1}{2}$, yielding a kernel of the class $C(\substack{3n\\n-\lambda},\tfrac{1}{2})$, namely,

$$x^{-n}\, I_n (\tfrac{1}{2}x)\, K_n (\tfrac{1}{2}x), \qquad \tfrac{1}{2}>R(n)>-\tfrac{1}{2}\dagger;$$

(ii) $\lambda=0$, $m=n$, $\mu=2n+\tfrac{1}{2}$, $\nu=2n-\tfrac{1}{2}$, yielding a C $(2n\pm\tfrac{1}{2})$, namely,

$$I_n (\tfrac{1}{2}x)\, K_n (\tfrac{1}{2}x),\quad R(n)>-\tfrac{1}{4};$$

(iii) $m=\tfrac{1}{2}$, $n=\tfrac{1}{4}+\tfrac{3}{4}\nu$, $\lambda=\tfrac{1}{4}-\tfrac{3}{4}\nu$, $\mu=\nu+1$, yielding a C $(\nu,\ \nu+1)$, namely,

$$x^{-\frac{3}{4}(1-\nu)}\,e^{-\frac{1}{4}x}\,I_{\frac{1}{4}+\frac{3}{4}\nu} (\tfrac{1}{2}x),\qquad R(\nu)>-1.$$

---

‡ T. M. MacRobert, *Quart. Jour of Math.*, 1940, 11, 98

For brevity $\Gamma_2(\lambda\pm\nu)$ is written for $\Gamma(\lambda+\nu)\,\Gamma(\lambda-\nu)$

§ G H Hardy, *Messenger of Math.*, 1918, 47, 178–84.

† The conditions necessary for the validity of the kernels are obtained from the consideration that R_ν functions are defined only for $R(\nu)>-1$

3. APPLICATION OF THESE KERNELS TO THE R_ν FUNCTION[*]

$$x^{\nu+\frac{1}{2}} e^{-\frac{1}{4}x^2} T_n^{2,0}(x^2), p = o \text{ OR A } +\text{VE INTEGER}$$

For this purpose we first evaluate the general integral

$$I = \int_0^\infty I_n\left(\tfrac{1}{2}xy\right) K_m\left(\tfrac{1}{2}xy\right)(xy)^\lambda y^{\nu+\frac{1}{2}} e^{-\frac{1}{4}y^2} T_p^{2,0}(y^2)\,dy.$$

Since $T_n^\mu(x) = \sum\limits_{r=0}^{n} \dfrac{(-)^m (-x)^r}{(n-r)!\,r!\,\Gamma(\nu+1+r)}$;

and[†]

$$K_\nu(z) = \tfrac{1}{2}\Gamma(\nu)\,\Gamma(1-\nu)\left\{I_{-\nu}(z) - I_\nu(z)\right\}$$

$$I_\lambda(2z)\,I_\mu(2z) = \frac{z^{\lambda+\mu}}{\Gamma(\lambda+1)\,\Gamma(\mu+1)}\,2F_3\left(\begin{matrix}\tfrac{1}{2}(1+\lambda+\mu),\ 1+\tfrac{1}{2}(\lambda+\mu);\\ 1+\lambda,\ 1+\mu,\ 1+\lambda+\mu;\end{matrix}\ 4z^2\right)$$

therefore

$$I = \frac{x^\lambda}{2\,\Gamma(n+1)}\sum_{r=0}^{2p}\frac{(-)^r}{r!\,(2p-r)!\,\Gamma(1+\nu+r)}\int_0^\infty y^{\lambda+\nu+2r+\frac{1}{2}}\,e^{-\frac{1}{4}y^2}\times$$

$$\left\{\begin{matrix}\dfrac{\Gamma(m)}{(\frac{1}{4}xy)^{m-n}}\ _2F_3\left(\begin{matrix}\tfrac{1}{2}(1+n-m),\ 1+\tfrac{1}{2}(n-m);\ \tfrac{1}{4}x^2y^2\\ 1+n,\ 1-m,\ 1+n-m;\end{matrix}\right)+\begin{matrix}\text{a similar function}\\ \text{with}\\ -m \text{ written for } m\end{matrix}\right\}dy.$$

$$\text{(3.1)}$$

Now by using the equivalent infinite series for the hypergeometric function $_2F_3$ and integrating term-by-term by means of the formula

$$\int_0^\infty y^{2m+1}\,e^{-\frac{1}{4}y^2}\,dy = 2^m\,\Gamma(1+m), \qquad R(m) > -1,$$

we have $I = \sum\limits_{r=0}^{2p}\left[(-)^r\,x^{m+\lambda/2}\,(2p-r)!\ \Gamma(1+\nu+r)\ \Gamma(1+n)\cdot 2^{\nu m+2-\frac{1}{2}m-r-k}\right.$

$$\left. \cdot\ \frac{\Gamma(k+r)\Gamma(m)}{(x/2\sqrt{2})^m}\ _3F_3\left(\begin{matrix}\tfrac{1}{2}(n-m+1),\ 1+\tfrac{1}{2}(n-m),\ k+r;\\ 1+n,\ 1-m,\ 1+n-m;\end{matrix}\ \tfrac{1}{2}x^2\right)+\begin{matrix}\text{a similar term with}\\ -m \text{ written for } m\end{matrix}\right]$$

$$= \phi(x), \text{ say,}$$

where $2k = \lambda + \nu + n - m + \tfrac{3}{2}$, $R(k) > 0$, and $R(m+k) > 0$.

The term-by-term integration effected in (3.1) is justified, since the $_2F_3$ is an integral fruction of y and its equivalent infinite series is therefore uniformly convergent in any arbitrary interval $(0, \alpha)$ and the remaining part of the integrand is positive, bounded and integrable in $(0, \alpha)$ and the complete integral I converges under the conditions stated.

* B. M. Wilson, *Messenger of Math.*, 1923–24, **53**, 157–60

† G. N. Watson, *Theory of Bessel Functions* (Camb., 1922), pp 78, 147. This treatise will henceforth be referred to as B.F.

We may now carry out the application of the various kernels by mere substitution in the final value $\phi(x)$ of I; but before we do so we have to ascertain the asymptotic behaviour of $\phi(x)$ in order to test the validity of the R_ν functions $f(x)$ by the convergence of the integral (1.1). For this we have recourse to the Mellin-Barnes' type of contour integral for $\phi(x)$. It is

$$\sum_{r=0}^{2p} A_r \, x^{n+\lambda-m} \int_s \frac{\Gamma(n-m+1+2s)\,\Gamma(r+k+2s)\,\Gamma(-s)\,\Gamma(m-s)}{\Gamma(n+1+s)\,\Gamma(n-m+1+s)} \left(\frac{x^2}{8}\right)^r ds,$$

where A_r is a constant independent of x.

We next alter the contour of integration so as to give us the asymptotic behaviour of $\phi(x)$. Carrying out the usual analysis we find that the leading terms in the asymptotic expansion are

$$ax^{-\nu-\frac{3}{2}} + bx^{\lambda-1}, \quad a, b \text{ being numerical constants.}$$

Evidently there are two ways of applying each kernel. Thus in the case of the first kernel we may put in $\phi(x)$, $m = n = -\lambda$ and either $\nu = 3n + \frac{1}{2}$ or $\nu = -n - \frac{1}{2}$, obtaining an $R_{-n-\frac{1}{2}}$ and an $R_{3n+\frac{1}{2}}$ function respectively. For instance, the former is

$$\sum_{r=0}^{2p} \{(-2)^r/r \, ! \, (2p-r) \, ! \, \Gamma(r+\tfrac{3}{2}n+\tfrac{3}{4})\} \, [\Gamma(r) \, \Gamma(n+r+1)\,(2\sqrt{2}/x)^n \times$$
$$\cdot {}_3F_2 \, (\tfrac{1}{2}, n+r+1; \; 1 \pm n; \; \tfrac{1}{4}x^2) + \Gamma(-n) \quad \Gamma(1+2n+r) \, (x/2\sqrt{2})^n$$
$$\times {}_3F_2 \, (n+\tfrac{1}{2}, 1+2n+r; \; 1+n, 1+2n; \; \tfrac{1}{4}x^2)], \quad \tfrac{1}{2} > \mathrm{R}\,(n) > -1. \quad (3.2)$$

The R_ν functions investigated in this way are all in the form of finite series of hypergeometric functions of the type ${}_3F_2\,(\tfrac{1}{4}x^2)$ obtained by the first two kernels and of the type ${}_3F_3$ obtained by the third. These reduce to a single pair of hypergeometric functions when $p = 0$ and these pairs in some cases are expressible in terms of the more common functions. Thus for instance (3.2) reduces when $p = 0$ to

$$x^{-1} W_{-\frac{1}{4}n, \, -\frac{1}{4}n}\,(\tfrac{1}{2}x^2) \, e^{\frac{1}{4}x^2}, \quad \tfrac{1}{2} > \mathrm{R}\,(n) > -1,$$

which is a special case of an R_ν function given by Bailey.[*]

4. TWO KERNELS OF THE TYPE $x^\lambda J_\nu\,(x/\sqrt{2})\,K_\nu\,(x/\sqrt{2})$

We shall first derive by the aid of Mellin's inversion theorem from the rule of § 1 a functional equation satisfied by infinite integrals of the kernels multiplied by x^{t-1}.

Since $\Gamma(a+i\beta t) \sim e^{-\frac{1}{2}\pi|\beta|t} \, t^{a-\frac{1}{2}}$ as $t \to \infty$ and $s = c + it$

[*] W. N. Bailey, *Jour. London Math. Soc.*, 1930, **5**, 258–65.

A3

it follows that as $|t| \to \infty$,

$$\phi(s) = \Gamma(\tfrac{1}{2}\nu + \tfrac{1}{4} + \tfrac{1}{2}s)\,\Gamma(\tfrac{1}{2}\mu + \tfrac{1}{4} + \tfrac{1}{2}s) \sim e^{-\tfrac{1}{2}\pi|t|}\,|t|^{\tfrac{1}{2}(\mu+\nu-1)+\sigma}.$$

Consequently supposing F (s) to be analytic and $o\left(e^{\tfrac{1}{2}(\pi-\epsilon)|t|},\ \epsilon > 0\right)$, c to be real, and > 0 we see that $\phi(s)$ F $(s) \to 0$ uniformly as $|t| \to \infty$ and the integral

$$\int_{-\infty}^{\infty} |\,\phi\,(c + it)\ \mathrm{F}\,(c + it)\,|\ dt$$

converges. Hence by Mellin's inversion theorem we have from (1·3)

$$f(s) = \int_{0}^{\infty} x^{s-1}\ \mathrm{P}\,(x)\ dx = 2^{s}\ \Gamma(\tfrac{1}{2}\nu + \tfrac{1}{2}s + \tfrac{1}{4})\ \Gamma(\tfrac{1}{2}\mu + \tfrac{1}{2}s + \tfrac{1}{4})\ \mathrm{F}\,(s)\ ds$$

and the relation F $(s) = $ F $(1-s)$ assumes the form of the functional equation

$$2^{1-s}\Gamma(\tfrac{1}{2}\nu + \tfrac{3}{4} - \tfrac{1}{2}s)\Gamma(\tfrac{1}{2}\mu + \tfrac{3}{4} - \tfrac{1}{2}s)\,f(s) = 2^{s}\Gamma(\tfrac{1}{2}\nu + \tfrac{1}{2}s + \tfrac{1}{4})\Gamma(\tfrac{1}{2}\mu + \tfrac{1}{2}s + \tfrac{1}{4})\,f(1-s) \quad (4)$$

showing that either side is an even function of $s - \tfrac{1}{2}$. The functional equation (4) is at times more convenient and serviceable to use for the investigation of kernels as illustrated below.

The special case $\mu = \nu$ and $a = b$ of the formula (1), B.F., p. 410, can be put after a slight change of the variable in the form

$$f(s) = \int_{0}^{\infty} x^{s-1}\ x^{\lambda}\ \mathrm{J}_{\rho}\left(\frac{x}{\sqrt{2}}\right)\ \mathrm{K}_{\rho}\left(\frac{x}{\sqrt{2}}\right)\ dx = \frac{\Gamma(\tfrac{1}{2}\rho + \tfrac{1}{2}\lambda + \tfrac{1}{2}s)\ \Gamma(\tfrac{1}{2}\lambda + \tfrac{1}{2}s)}{\Gamma(\tfrac{1}{2}\rho - \tfrac{1}{2}\lambda - \tfrac{1}{2}s + 1)\,(2\sqrt{2})^{s-\lambda-\nu}},$$

$$\mathrm{R}\,(s + \lambda + \rho) > |\,\mathrm{R}\,(\rho)\,|.$$

In order that this might give us a kernel, the functional equation to be satisfied is

$$\phi(s)\,\psi(1-s) = \psi(s)\,\phi(1-s)$$

where

$$\psi(s) = \Gamma(\tfrac{1}{2}\rho + \tfrac{1}{2}s + \tfrac{1}{2}\lambda)\ \Gamma(\tfrac{1}{2}s + \tfrac{1}{2}\lambda)\ \Gamma(\tfrac{1}{2}\rho - \tfrac{1}{2}\lambda + \tfrac{1}{2}s + \tfrac{1}{2})$$

and

$$\phi(s) = \Gamma(\tfrac{1}{2}\nu + \tfrac{1}{2}s + \tfrac{1}{4})\ \Gamma(\tfrac{1}{2}\mu + \tfrac{1}{2}s + \tfrac{1}{4}).$$

The following solutions are possible :—

(i) $\lambda = \tfrac{1}{2},\ \mu = 0,\ \rho = \tfrac{1}{2}\nu$, yielding a C $(0, 2\nu)$, namely,

$$x^{\tfrac{1}{2}}\ \mathrm{J}_{\nu}\left(\frac{x}{\sqrt{2}}\right)\ \mathrm{K}_{\nu}\left(\frac{x}{\sqrt{2}}\right),\qquad \mathrm{R}\,(\nu) > -\tfrac{1}{2};$$

(ii) $\lambda = \tfrac{3}{2},\ \mu = 2,\ \rho = \tfrac{1}{2}\nu$, yielding a C $(2, 2\nu)$, namely,

$$x^{\tfrac{3}{2}}\ \mathrm{J}_{\nu}\left(\frac{x}{\sqrt{2}}\right)\ \mathrm{K}_{\nu}\left(\frac{x}{\sqrt{2}}\right),\qquad \mathrm{R}\,(\nu) > -\tfrac{1}{2}.$$

5. APPLICATION OF THE KERNELS OF § 4 TO THE R_ν FUNCTION $x^{\frac{1}{2}} J_\nu (\frac{1}{2}x^2)$

Taking the corresponding R_0 function for the application of the first kernel and making use of the integral*

$$\int_0^\infty 2y \, J_\nu (y\sqrt{2}) \, K_\nu (y\sqrt{2}) \, J_0 (y^2|2\lambda) \, dy = \lambda \, I_{\frac{1}{2}\nu} (\lambda) \, K_{\frac{1}{2}\nu} (\lambda) \qquad (5\cdot1)$$

we are led to the R_ν function

$$\sqrt{x} \, I_{\frac{1}{2}\nu} (\tfrac{1}{4}x^2) \, K_{\frac{1}{2}\nu} (\tfrac{1}{4}x^2), \quad R (\nu) \_> -1,$$

a result due to Erdélyi.‡

Applying the second kernel to the corresponding R_2 function we obtain the $R_{3\nu}$ function

$$g(x) = \int_0^\infty (xy)^{\frac{1}{2}} \, J_\nu \left(\frac{xy}{\sqrt{2}} \right) \, K_\nu \left(\frac{xy}{\sqrt{2}} \right) \, y^{\frac{1}{2}} \, J_1 (\tfrac{1}{2}y^2) \, dy.$$

To evaluate this integral we differentiate† both the sides of $(5\cdot1)$ with respect to λ and use the recurrence formulæ (B.F , § 3·71) and the formula

$$I_\nu (z) \, K_{\nu+1} (z) + I_{\nu+1} (z) \, K_\nu (z) = 1/z$$

and obtain finally the R_ν function

$$g(x) = (1 - \tfrac{1}{2}\nu) \, x^{\frac{1}{2}} \, I_{\frac{1}{2}\nu} (\tfrac{1}{4}x^2) \, K_{\frac{1}{2}\nu} (\tfrac{1}{4}x^2) - x^{\frac{5}{2}} + \tfrac{1}{2}x^{\frac{5}{2}} \, I_{\frac{1}{2}\nu-1} (\tfrac{1}{4}x^2) \, K_{\frac{1}{2}\nu} (\tfrac{1}{4}x^2)$$

If we use the asymptotic expansions (B.F., § 7·23)

$$K_\nu (x) \sim \sqrt{\frac{\pi}{2x}} \, e^{-x} \left[1 + \frac{4\nu^2 - 1}{8x} + \frac{(4\nu^2 - 1)(4\nu^2 - 9)}{2!(8x)^2} + \cdots \right]$$

and

$$I_\nu (x) \sim \frac{e^x}{\sqrt{2\pi x}} \left[1 - \frac{4\nu^2 - 1}{8x} + \frac{(4\nu^2 - 1)(4\nu^2 - 9)}{2!(8x)^2} - \cdots \right]$$

we find after some calculation that the leading term in the asymptotic expansion of $g(x)$ is $x^{-3/2}$. Consequently $g(x)$ is R_ν if $R(\nu) > -1$.

We conclude by giving two other kernels investigated by this method. They are of the class $C(\nu, \nu+1)$ valid for $R(\nu) > -1$.

(i) $x^{\nu-m} \, e^{\frac{1}{4}x} \, W_{3m-3\nu-\frac{1}{4}, \, m} (x)$, (ii) $x^{\nu+\frac{1}{4}} \, e^{-x} \, T_{2\nu+1}^{2n} (2x)$.

Two special cases of (i), viz., for $m = \pm \frac{1}{4}$ are

$$x^{\nu+\frac{1}{4}} \, e^{\frac{1}{4}x} \, D_{-\nu-\frac{1}{4}} (\sqrt{2x}) \quad \text{and} \quad x^\nu \, e^{\frac{1}{4}x} \, D_{-4\nu-\frac{1}{4}} (\sqrt{2x}).$$

---

* S. C. Mitra, *Bulletin Calcutta Math. Soc.*, 1933–34, **25**, 89.

‡ A. Erdélyi, *Jour Lond Math. Soc*, 1938, **13**, 153

† A process easily justified by the uniform and absolute convergence of the integrals involved

BENDING OF AN EQUILATERAL PLATE

By B. R. Seth

(From the Department of Mathematics, Hindu College, Delhi)

1. One of the most important of the special problems of Elasticity is the bending of plates. It has received incessant attention from many quarters.[1] The form of boundaries which have been considered are a circle, an ellipse, a rectangle, half an ellipse bounded by the transverse axis and a sector of a circle. The solutions for a circle and an ellipse are simple in character. The literature available for a rectangle can form the subject-matter of a good treatise. It will therefore be not devoid of interest to give an exact solution for an equilateral plate.

2. We assume that the plate has its four edges supported and is bent by uniform pressure applied to one face. Let (u, v, w) be the displacement of any point of the middle plane. We take the face subjected to pressure to be $z = -h$. Let p be the load per unit area and $D = \frac{2}{3} E h^3 / (1 - \sigma^2)$, the flexural rigidity of the plate, F, h, σ having their usual meanings. Then, we know that w at any point $(x, y, 0)$ satisfies the differential equation[2]

$$D \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right)^2 w = D \nabla_1^4 w = p. \tag{1}$$

The boundary conditions can be put in the form

$$w = 0, \quad \nabla_1^2 w = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) w = 0, \tag{2}$$

over all the three edges.

We can put (1) in the form

$$\nabla_1^2 \left[\nabla_1^2 w - \frac{1}{4} \frac{p}{D} (x^2 + y^2) \right] = 0. \tag{3}$$

If therefore we put

$$\psi = \nabla_1^2 w - \frac{1}{4} \frac{p}{D} (x^2 + y^2), \tag{4}$$

we see that ψ satisfies $\nabla_1^2 \psi = 0$ and assumes the value $-\frac{1}{4} \frac{p}{D} (x^2 + y^2)$ over the boundary. The problem is now the same as that of the torsion of an equilateral prism, whose solution is known.

3. Let the edges of the plate be given by $y = a$, $y = \pm \sqrt{3}x$, then we know that

$$\psi = \tfrac{1}{2}\frac{p}{D}(x^2 - y^2) + \frac{1}{4a}\frac{p}{D}(y^3 - 3x^2y), \qquad (4\cdot1)$$

so that

$$\nabla_1^2 w = \tfrac{1}{2}\frac{p}{D}(x^2 + y^2) + \tfrac{1}{2}\frac{p}{D}(x^2 - y^2) + \frac{1}{4a}\frac{p}{D}(y^3 - 3x^2y)$$

$$= \tfrac{1}{2}\frac{p}{Da}(y - a)(y^2 - 3x^2). \qquad (5)$$

If ϕ is harmonic, then

$$\nabla_1^2(x\phi) = 2\frac{\partial\phi}{\partial x}, \ \nabla_1^2(y\phi) = 2\frac{\partial\phi}{\partial y}.$$

We can now re-write (5) as

$$\nabla_1^2\left[w - \tfrac{1}{8}\frac{p}{D}x^2y^2 - \tfrac{1}{12}\frac{p}{D}y(3x^2y - y^3) + \frac{1}{8a}\frac{p}{D}x(xy^2 - x^3y)\right] = 0, \quad (6)$$

which shows that

$$w = \tfrac{1}{8}\frac{p}{D}x^2y^2 + \tfrac{1}{12}\frac{p}{D}y(3x^2y - y^3) + \frac{1}{8a}\frac{p}{D}x(xy^2 - x^3y) + w_0, \quad (6\cdot1)$$

when w_0 is harmonic. Since w is to vanish over $y = a$ and $y = \pm \sqrt{3}x$, we put

$$w_0 = A_1(3x^2y - y^3) + A_2(x^4 - 6x^2y^2 + y^4)$$
$$+ A_3(5x^4y - 10x^2y^3 + y^5). \qquad (6\cdot2)$$

The boundary condition $w = 0$ over the sides is found to be satisfied if we take

$$A_1 = -\tfrac{1}{48}\frac{pa}{D}, \ A_2 = \tfrac{3}{64}\frac{p}{D}, \ A_3 = \tfrac{1}{64}\frac{p}{Da}$$

The value of w is therefore

$$w = \tfrac{1}{8}\frac{p}{D}x^2y^2 + \tfrac{1}{12}\frac{p}{D}y(3x^2y - y^3) + \frac{1}{8a}\frac{p}{D}x(xy^2 - x^3y)$$

$$+ \tfrac{3}{64}\frac{p}{D}(x^4 - 6x^2y^2 + y^4) + \frac{1}{64}\frac{p}{Da}(5x^4y - 10x^2y^3 + y^5)$$

$$- \tfrac{1}{48}\frac{pa}{D}(3x^2y - y^3)$$

$$= \frac{1}{192}\frac{p}{Da}(a - y)(3x^2 - y^2)(3x^2 + 3y^2 - 4ay). \qquad (7)$$

From (7) we see that w vanishes over all the three sides and also on the circle

$$x^2 + \left(y - \frac{2a}{3}\right)^2 = \frac{4a^2}{9},$$

which is the circumcircle of the triangle. w therefore does not vanish at any other point of the plate except at the edges.

If w_c denotes the deflection at the centre of the plate given by $x = 0$, $y = \frac{2}{3} a$, we find

$$w_c = \frac{1}{4 \cdot 3^5} \frac{pa^4}{D} \qquad (8)$$

To get the extreme value of w we put $\frac{\partial w}{\partial x} = 0$, $\frac{\partial w}{\partial y} = 0$. The first condition gives

$$x = 0, \text{ or } y = a, \text{ or } 3x^2 + y^2 - 2ay = 0, \qquad (9\cdot1)$$

which combined with the second gives the following points:

$$\left(\pm \frac{4a}{5\sqrt{3}}, \frac{2a}{5}\right), (0, 0), \left(\pm \frac{a}{\sqrt{3}}, a\right), \left(0, \frac{2a}{3}\right), \left(0, \frac{2a}{3}\right).$$

The only admissible value, besides $(0, 0)$, $(\pm a/\sqrt{3}, a)$, which are the vertices of the plate, is $(0, \frac{2}{3} a)$. The maximum value of w therefore occurs at the centre of the plate, and hence if w_m denotes this value,

$$w_m = w_c = \frac{1}{4 \cdot 3^5} \cdot \frac{pa^4}{D} \qquad (9)$$

For a circular plate of radius c the corresponding value of w is[3]

$$w = \frac{1}{64} \frac{p}{D} (c^2 - r^2) \left(\frac{5 + \sigma}{1 + \sigma} c^2 - r^2\right), \qquad (10)$$

and hence

$$w_{r1} = w_{m1} = \frac{1}{64} \frac{p}{D} \cdot \frac{5 + \sigma}{1 + \sigma} c^4. \qquad (10\cdot1)$$

If, therefore, we take the in-circle of the plate for which $c = \frac{1}{3} a$, we find

$$\frac{w_c}{w_{c1}} = \frac{w_m}{w_{m1}} = \frac{16 (1 + \sigma)}{3 (5 + \sigma)}, \qquad (10\cdot2)$$

which for $0 < \sigma < \frac{1}{2}$ varies between $1\cdot07$ and $1\cdot46$.

4. For a thin plate the flexural couple G is given by

$$G = - D \left\{\frac{\partial^2 w}{\partial \nu^2} + \sigma \frac{\partial^2 w}{\partial s^2}\right\} \qquad (11)$$

where s is measured along any curve drawn on the middle surface and ν is the direction of the normal to this curve. Let s be measured along

$y =$ const., then (11) becomes

$$G = - D \left[\nabla_1{}^2 w - (1 - \sigma) \frac{\partial^2 w}{\partial x^2} \right]. \qquad (11 \cdot 1)$$

We find

$$\frac{\partial^2 w}{\partial x^2} = \frac{1}{16} \frac{p}{Da} (a - y) (9x^2 + y^2 - 2ay), \qquad (12)$$

and $\nabla_1{}^2 w$ is given by (6). Hence

$$G = - \frac{1}{16} \frac{p}{a} (a - y) [4 (3x^2 - y^2) - (1 - \sigma) (9x^2 + y^2 - 2ay)] \quad (13)$$

G vanishes over $y = a$, as it should.

For a thick plate a term of the type

$$h^2 \frac{\partial^2}{\partial x^2} (\nabla_1{}^2 w) = \frac{3}{2} h^2 \frac{p}{Da} (a - y), \qquad (13 \cdot 1)$$

should be added to (13). This also vanishes for $y = a$. Hence G vanishes whether the plate is thick or thin. Since there is symmetry G vanishes over the remaining two edges as well.

For extreme values of G we get

$$(a - y) [24x - 18x (1 - \sigma)] = 0,$$

$$\textit{i.e.,} \quad y = a, \; x = 0,$$

and

$$4 (3x^2 - y^2) - (1 - \sigma) (9x^2 + y^2 - 2ay)$$
$$+ (a - y) [8y + (1 - \sigma) (2y - 2a)] = 0.$$

The possible points are given by

$$\left[\pm \sqrt{\frac{3 + \sigma}{5 (1 + 3\sigma)}} \, a, \; a \right], \; \left[0, \; \frac{a (7 - 3\sigma) \pm a \sqrt{19 - 6\sigma + 3\sigma^2}}{3 (5 - \sigma)} \right].$$

The only admissible value is

$$0, \; \frac{a (7 - 3\sigma) + a \sqrt{19 - (\sigma + 3\sigma^2}}{3 (5 - \sigma)}, \qquad (14)$$

which for $0 < \sigma < \frac{1}{2}$ varies between $(0, 0 \cdot 72a)$ and $(0, 0 \cdot 76a)$. Thus the points of greatest weakness are on the medians and are very near the centre of the plate. For $\sigma = \frac{1}{3}$ the maximum value of G is found to be approximately $\frac{1}{40} pa^2$.

The other stress couple H is

$$H = D (1 - \sigma) \frac{\partial}{\partial r} \left(\frac{\partial w}{\partial s} \right). \qquad (15)$$

and for $y =$ constant, it is

$$H = D (1 - \sigma) \frac{\partial^2 w}{\partial x \, \partial y} = -\frac{1}{16} \frac{p}{a} (1 - \sigma) \, x \, [3 (x^2 + y^2) - 4ay + 2a^2],$$

which shews that it vanishes along all the medians.

The shearing force N is

$$N = - D \frac{\partial}{\partial y} (\nabla_1^2 w), \qquad (16)$$

and for $y =$ constant, it is

$$N = - D \frac{\partial}{\partial y} (\nabla_1^2 w) = \frac{1}{4} \frac{p}{a} (3x^2 - 3y^2 + 2ay). \qquad (16 \cdot 1)$$

This vanishes at all the angular points. For a thick plate N remains as given in $(16 \cdot 1)$. But a term of the type in $(16 \cdot 1)$ has to be added to H given in $(15 \cdot 1)$.

w being known, the displacements (u, v) can now be easily obtained.

Other cases of supported and clamped plates will be discussed in another paper.

5. SUMMARY

An exact solution is obtained for an equilateral plate supported at its edges and bent by uniform pressure. It is found that the maximum deflection occurs at the centre and that its value is $pa^4/4 \cdot 3^5 D$. The points of greatest weakness are found to be very near the centre, the maximum value of the flexural couple G for $\sigma = \frac{1}{3}$ being approximately $\frac{1}{40} pa^2$.

REFERENCES

1. Love   .   *Theory of Elasticity*, 1927, 4th ed., Chap. XXII. He gives
                      many references.

   Nadai, A.   .   " Die elastischen Platten," *Julius Springer, Berlin*, 1925.

   Holl, D. L.   .. *Iowa State College Engr. Exp. Sta. Bul.*, 1936, 129. He gives
                      many references to the work of Westergaard, Spangler and
                      others

   Timoshenko, S. P .   *Proc. 5th International Congress of Appl. Mech.*, 1938, 40–43.

   Gran Olsson and Reissner, E. *J of Math. and Phys*, 1940, 19, 131–39.

   Woinowsky-Krieger, S .. *Ing. Arch.*, 1933, 4, 203–66, 303–31

   Stevenson, A. C. .. *Phil Mag.*, 1943, 34, 105–14.

   Sokolnikaff, I. S .. *Bull Amer. Math. Soc*, 1942, 48, 539–55

   Stoker, J J   .   *Ibid*, p. 247

   Reissner, E   .. *J. of Math and Phys*, 1944, 23, 184–91.

2. Love   .. *Loc. cit.*, p. 484.

3. Love   .. *Ibid.*, p. 490.

SYNTHESIS OF AMMONIA FROM ACTIVE NITROGEN

By K. VENKATESWARA RAO, M.Sc.

(Research Scholar, Chemistry Department, Benares Hindu University)

LEWIS[1] was the first to synthesise ammonia from active nitrogen and hydrogen; the activation of the latter was considered essential for the change. Dixon and Steiner[2] observed that the reaction was greatly accelerated by nickel, iron or copper. According to them, adsorbed hydrogen reacted with nitrogen atoms giving ammonia, the relative yield being independent of the area of the catalyst. Joshi and Purushotham[3] found that active nitrogen was deactivated by " the continued operation of the exciting field " and also by hydrogen, even in small proportions. That mixtures of active nitrogen and hydrogen under electric discharge would yield ammonia, therefore, appeared unlikely. Joshi and Purushotham (*loc. cit.*) developed a novel method for obtaining ammonia, *viz.*, by subjecting the catalyst to alternate streams of active nitrogen and hydrogen. Any unstable nitride or labile compound of nitrogen formed was expected to react with hydrogen and give ammonia. This last was separated from the effluent hydrogen by freezing out with liquid air; it was estimated colorimetrically using Nestler's solution.

The object of the present work was to investigate the precise working conditions for the production of ammonia by the above process and also to eliminate the use of liquid air for ammonia estimation.

EXPERIMENTAL

The experimental arrangement (Fig. 1) was essentially similar to that adopted by Joshi and Purushotham. It consisted chiefly of a Crookes tube, D, with aluminium electrodes, connected to a high capacity condenser and excited by a potential, V, obtained from an induction coil. Nitrogen and hydrogen used in these experiments were obtained from cylinders. Nitrogen was purified carefully by bubbling through B_1 and B_2 filled with alkaline pyrogallol in order to remove oxygen; it was stocked in the aspirator A_1. Similarly, hydrogen was led through a water bubbler, B_3 (to indicate the rate at which hydrogen was admitted in the aspirator) and stocked in A_2. Through a series of drying tubes and control stop-cocks, to regulate the gas pressure, the aspirators were connected to a glass spiral S, the discharge tube D, an observation vessel O, a trap for collecting ammonia C, and a Cenco pump in series. A weighed amount of the substance (2 gm.) under examination was put in a porcelain boat and
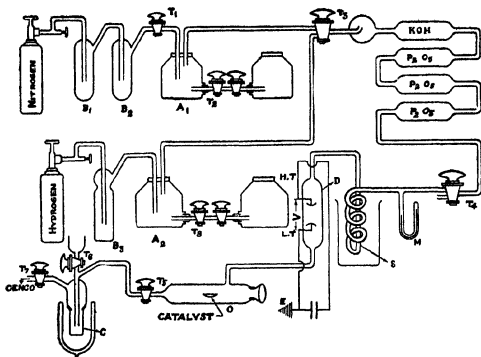
Fig 1. Ammonia Synthesis from Active Nitrogen

placed in O, and the apparatus was then evacuated from T_5 to T_7. By opening the stop-cock T_3 to the aspirator A_1, nitrogen was allowed to pass through the drying tubes; its pressure was regulated by the stop-cock T_4. The manometer, M, served to indicate the pressure of the streaming gas. It was found by trials that preheating nitrogen before activation in the discharge tube increased appreciably the yield of ammonia. The glass spiral S and the observation vessel O were maintained at a temperature of 200° C. and 80° C. respectively.

Nitrogen preheated in the glass spiral and activated by a condensed electric discharge was then allowed to flow at a constant pressure and interact with the heated catalyst for half an hour. This was then replaced by a current of hydrogen, at a slightly higher pressure, under otherwise identical conditions for an equal duration. The effluent gases were bubbled through a standard sulphuric acid solution. From the amount of acid neutralised (column iii, Table I) found by back titration with a standard alkali, the ammonia formed was ascertained.

Table I gives details for typical catalysts with which the ammonia yield was found to be maximum and minimum. Each experiment was

conducted at least twice to test the reproducibility of the results. The catalysts were generally selected from amongst those substances which (a) showed an induced luminosity when placed in the after-glow of the streaming gas, (b) from nitrides easily, and (c) ' sorb ' gases.

TABLE I

Substance	Strength of the acid	Volume of the acid reacted (c.c.)	Weight of ammonia (mgm.)
Alloy of Tin and Lead (20% tin)	0·1154 N	1·37	2·7
,, ,,	,,	0·8	1·6
Magnesium	,,	0·8	1·6
,,	,,	0·83	1·62
Rose metal	0·09065 N	0·81	1·3
,,	,,	0·8	1·2
Lead	0·09201 N	0·15	0·2
,,	,,	0·15	0·2

TABLE II

No.	Substance	Wt. of ammonia mgm.	No.	Substance	Wt. of ammonia mgm.
1	Sulphur	1·0	28	Magnesium oxide	0·7
2	Arsenic	0·9	29	Magnesium phosphate	0·4
3	Lithium carbonate	0·9	30	Magnesium carbonate	0·4
4	Starch	0·9	31	Magnesium sulphate	0·4
5	Lithium benzoate	0·8	32	Bismuth sulphate	1·0
6	Cadmium tungstate	0·6	33	Mercarous sulphate	1·0
7	Dextrose	0·5	34	Cerium sulphate	0·9
8	Lithium phosphate	0·3	35	Strontium sulphate	0·7
			36	Barium sulphate	0·7
9	Magnesium	1·6	37	Calcium sulphate	0·4
10	Tungsten	1·5	38	Hypo	0·8
11	Tin	1·2	39	Potassium alum	0·5
12	Iron	0·9			
13	Cobalt	0·9	40	Borax	1·1
14	Silicon	0·9	41	Lead borate	1·1
15	Antimony	0·9	42	Iron oxalate	1·0
16	Selenium	0·8	43	Cobalt oxalate	0·5
17	Copper	0·6	44	Nickel oxalate	0·4
18	Aluminium	0·5	45	Mercurous cyanide	0·8
19	Cadmium	0·5	46	Cuprous cyanide	0·7
20	Zinc	0·8	47	Potassium ferrocyanide	0·5
21	Chromium	0·4	48	Antimony trioxide	0·8
22	Lead	0·2	49	Vanadium pentoxide	0·7
23	Activated carbon	0·3	50	Iron oxide	0·7
			51	Cobalt oxide	0·5
24	Alloy of tin and lead (25% Sn)	2·7	52	Aluminium carbide	1·1
25	Rose metal	1·3	53	Barium borate	0·9
			54	Barium arsenate	0·7
26	Magnesium tartrate	1·0	55	Monazite	0·4
27	Magnesium borate	0·7			

DISCUSSION

An attempt to arrange the catalysts which gave good yields of ammonia, in the order of activity shows: alloy of tin and lead > magnesium >

tungsten > rose metal > tin. It is interesting to note that of all the metals examined (Table II) magnesium gives the maximum yield of ammonia, perhaps, due to its markedly greater affinity for nitrogen as revealed both by ready nitride formation and especially heavy 'sorption'. A remarkable feature of the present method is that the activity of the catalyst remains unimpaired even after prolonged use, except in the case of the tin-lead alloy which has been found to give greater yield than any other substance. The foregoing results (Table II) not only show the utilisability of active nitrogen for ammonia synthesis with a wide range of catalysts but also that this method may be developed into a continuous operation as required in a large-scale process.

Lithium phosphate glows brilliantly in presence of active nitrogen, lead forms the nitride easily and activated carbon is noted for its ' sorption ' of gases. The extremely low yields obtained with these substances is therefore very significant According to Joshi and Purushotham, the primary reaction would appear to be the formation of an unstable nitride or an adsorption complex when the catalyst is exposed to active nitrogen. Subsequently, this reacts with hydrogen to give ammonia. As such, the efficiency of the catalyst, perhaps, depends not so much on its reaction with active nitrogen, as on its reactivity towards hydrogen. This explains the comparatively low yields obtained with lithium phosphate and other substances referred to above, since the corresponding nitrides are stable. It would appear that a chief condition for increasing the ammonia yield is that the nitride formed must be unstable under the working conditions.

SUMMARY

Following the preliminary work of Joshi and Purushotham, the utilisability of active nitrogen for ammonia synthesis has been investigated in respect of 55 catalysts. These, when exposed to active nitrogen under certain conditions of temperature and pressure, form unstable nitrides or/and adsorption complexes, which react with hydrogen streamed subsequently so as to give ammonia. Yields were largest with tin-lead alloy > magnesium > tungsten > rose metal > tin.

REFERENCES

1. Lewis   .. J Amer. Chem. Soc., 1928, 50, 27.
2. Dixon and Steiner   . Z. Physikal Chem., (B), 1931, 14, 397.
3. Joshi and Purushotham   .. Curr. Sci., 1940, 9, 534.

PAIRS OF SYMMETRIC AND SKEW MATRICES IN AN ARBITRARY FIELD—I

BY K. VENKATACHALIENGAR

(Department of Mathematics, Central College, Bangalore)

INTRODUCTION

THE problem of the congruent reduction of a pair or pencil of symmetric matrices and the finding of the criteria for the congruence of two such pairs was solved by Weierstrass in the case of an algebraically closed field. Dickson (Dickson, I) solved the same problem for any field of characteristic zero. He obtained the criteria as the congruence of two single diagonal matrices in appropriate algebraic fields. Recently Williamson (Williamson, I, II, III)* solved this problem together with those concerning (1) *skew-skew* pairs—*i.e.*, when both the matrices are skew, and (2) *symskew* pairs—*i.e.*, when one of the matrices is skew and the other is symmetric. He has stated that he takes the field as having the characteristic zero, although his method is probably applicable to all *infinite* fields of any characteristic other than 2.

In the present paper these problems have been solved for all fields of characteristic other than 2 (*including strictly finite fields also*) by a new simple method of a more genetic character than those employed earlier. New canonical forms are found which have enabled the extension to any field the classic results concerning the nature of the elementary divisors of a pair in the real number field when the quadratic form corresponding to one of the matrices is ±ve definite. The singular pair is treated by a new method which is applicable to fields of characteristic 2 also (congruent reduction into irreducible components only). The complete structure of the linear transformations which carry a given non-singular pair into itself has been obtained and the group of all such transformations, after we omit some exceptional ones is shown to be rational-parametric.

This problem is of greater complexity when the field is of characteristic 2. Congruent reduction and some allied problems of single symmetric matrices have been considered by Albert in a recent paper (Albert I).

---

* The papers of Williamson were available to the author only in their summarised reviews in *Zentral Blatt für Math*.

Adopting his definitions of symmetric and skew matrices the problem of congruent reduction of a given pair (for fields of characteristic 2) has been solved completely; for the congruence of two given pairs, some necessary criteria only have been obtained. It is interesting to find that even if the elementary divisors of two pairs are identical it does not always happen that the orders of their irreducible components are the same, as is always the case when the characteristic is not 2; and that the direct sum of two irreducible components may reduce to the sum of three such ones. A similar phenomenon was observed by Albert (*loc. cit.*) in the case of a single symmetric matrix. The congruent reduction of a singular pair into the sum of singular and non-singular irreducible components has also been obtained. It is proved that if two singular pairs are congruent, the same is also true of the direct sums of all their singular and all their non-singular components as was shown by Dickson (*loc. cit.*) for fields of characteristic other than 2. Criteria for congruence have been obtained in some particular cases and some of the results in (Albert I) concerning the orthogonal equivalence of two symmetric matrices have also been derived as particular cases of more general results.

By the same genetic method the problem has been solved for the case of pairs $\lambda A + \mu B$ where A is symmetric, and B transforms A, congruently, to its inverse; in particular A may be the unit matrix and B an orthogonal one. The criteria for the congruence of two such pairs are of the same nature. As a particular case, the criteria for the orthogonal equivalence of two orthogonal matrices for a field of characteristic other than 2, have also been obtained.

NOTATION AND SOME DEFINITIONS

$A = |\, a_{rs}\,|$, $B = |\, b_{rs}\,|$ denote square matrices. The determinant of A is denoted by $|\,A\,|$ or $\|\, a_{rs}\,\|$. The transpose of A is denoted by A'. The vectors or *one-column-matrices* of the carrier-space in which the matrices induce the corresponding linear transformations are denoted by ξ, η, ρ, etc. The direct sum of two (or more) matrices A and B is denoted by $A \dotplus B$; *i.e.*,

$$\begin{pmatrix} A & 0 & 0 \\ 0 & B & 0 \\ 0 & 0 & C \end{pmatrix} = A \dotplus B \dotplus C$$

A pair or pencil $\lambda A + \mu B$ is called (1) a *sym-sym* pencil if A and B are both symmetric, (2) a *skew-skew* pencil if both of them are skew, (3) a *sym-skew* pencil if one of them is symmetric and the other is skew.

Two sub-spaces R_1 and R_2 are said to be conjugate w.r.t. a symmetric or skew matrix A, if for any two vectors ξ_1 and ξ_2 of R_1 and R_2 respectively,

$$\xi_1' A \xi_2 = 0,$$

where ξ_1' is the *transpose* of ξ_1, or it is the corresponding one row-matrix.

§1. REDUCTION OF A SYM-SYM PENCIL IN A FIELD OF CHARACTERISTIC OTHER THAN 2

*1·1. Let $\lambda A + \mu B$ be a *sym-sym* pair or pencil. We take the field of coefficients k to be an arbitrary one of characteristic other than 2 and proceed to obtain the congruent reduction of the pair into the direct sum of components, *viz.*, the determination of a non-singular matrix T satisfying the following equation·

$$\text{T} (\lambda A + \mu B) \text{ T}' = (\lambda A_1 + \mu B_1) \dotplus (\lambda A_2 + \mu B_2) \dotplus \ldots \dotplus (\lambda A_k + \mu B_k). \quad (1)$$

If the components on the R.H S of (1) are not reducible further, they are called the irreducible components of $\lambda A + \mu B$. If $\lambda A^* + \mu B^*$ is another given pair and if T exists so that

$$\text{T} (\lambda A + \mu B) \text{ T}' = \lambda A^* + \mu B^* \quad (2)$$

we say that the two pairs are congruent and the criteria for the same will be obtained in a subsequent section.

1·2. The transformation $(\lambda A + \mu B) \rightarrow \text{T} (\lambda A + \mu B) \text{ T}'$ can be looked upon as the transformation induced in the corresponding pencil of quadratic forms $\xi' (\lambda A + \mu B) \xi, \ldots$ by the transformation of the co-ordinate vectors of the carrier space by means of the linear transformation T'. If $\xi_1, \xi_2, \ldots \xi_n$ are the new co-ordinate vectors, then it is clear that

$$\lambda a_{rs}^* + \mu b_{rs}^* = \xi_r' (\lambda A + \mu B) \xi_s \quad (3)$$

where $\lambda A^* + \mu B^* = | \lambda a_{rs}^* + \mu b_{rs}^* |$. If B is non-singular and

$$J = B^{-1} A \quad (4)$$

the mapping J is changed over into $(\text{T}')^{-1} J \text{T}'$ or into the form it would assume in the new coordinate system. It is also clear that a relation of the following form.

$$A\xi = B\eta \quad (5)$$

is retained by all congruent transformations, even if $| A | = | B | = 0$. If ψ is any polynomial in J, $B\psi$ and $A\psi$ are also symmetric and for any two vectors ξ and η

$$\xi' B\eta = \eta' B\xi \quad (6)$$

246 K. Venkatachaliengar

and that

$$(f\xi)' B\psi\eta = \eta' B\psi f\xi = \xi' B\psi f\eta \qquad (7)$$

where f is also a polynomial in J. The equations (6) and (7) are frequently employed in the sequel. We first consider the case when one of the matrices of the pencil is non-singular and prove the following theorem of reduction.

THEOREM 1·3·1.—Let one of the matrices, say B of the *sym-sym* pencil, be non-singular and the splitting of the minimum polynomial of $J = B^{-1} A$ into relatively prime factors be $\phi^r \phi_1^{r_1} \ldots \phi_s^{r_s}$. Then $(\lambda A + \mu B)$ can be congruently reduced to the direct sum

$$(\lambda A + \mu B) = (\lambda A_1 + \mu B_1) \dot{+} (\lambda A_1{}^* + \mu B_1{}^*)$$

where $(\lambda A_1 + \mu B_1)$ is the irreducible component corresponding to ϕ^r, *i.e.*, the minimum-polynomial of $J_1 = B_1^{-1} A_1$ is ϕ^r.

Proof.—Let ξ, $\eta, \ldots$ etc., represent the vectors of the carrier-space R_n with the matrices induce the corresponding linear transformations. Let the minimum-polynomial of J be written as $\phi^r f$ where f is prime to the (irreducible) polynomial ϕ. Let us write for brevity $\phi, f, \ldots$ for ϕ (J), f(J)..., etc. Now the symmetric matrix

$$B\phi^{r-1} f^2 = {}_s B\phi^{r-1} (J) f^2 (J) \qquad (8)$$

is not zero; for if it were so $\phi^{r-1} f^2 = B^{-1} \cdot B\phi^{r-1} f^2 = 0$, contradicting the fact that $\phi^r f$ is the minimum-polynomial of J. As the characteristic is not 2, a vector ξ exists for which

$$\xi' B\phi^{r-1} f^2 \xi \neq 0. \qquad (9)$$

Utilising the equations (6) and (7) we can write (9) as

$$\eta' B\phi^{r-1} \eta \neq 0 \qquad (10)$$

for the vector $\eta = f\xi$, *i.e.* f (J) ξ. We also have

$$\phi^r \eta = \phi^r f\xi = 0 \qquad (11)$$

as $\phi^r f$ is the minimum-polynomial of J. Let the degree of ϕ be m. Then *the rm vectors*

$$J^p \phi^q \eta, \ 0 \leqslant p < m, \ 0 \leqslant q < r \qquad (12)$$

are linearly independent; for, if they are not so an equation of the following form holds

$$\sum_{i=0}^{r-1} f_i \phi^i \eta = 0 \qquad (13)$$

where the f_i are polynomials of degree $< m$ in J. Let f_k be the first polynomial among them which is not zero. As ϕ is irreducible a

polynomial ψ exists so that

$$\psi f_k \equiv 1 \pmod{\phi}. \tag{14}$$

After multiplying (13) on the left by ψ we obtain a relation of the following form

$$\phi^k \eta = \phi^{k+1} \, \mathbf{F}\eta \tag{15}$$

where $\mathbf{F}$ is some polynomial (of degree not necessarily $< m$). We derive

$$\eta' \mathbf{B}\phi^{r-1}\,\eta = \eta' \mathbf{B}\phi^{r-k-1}\,\phi^k\eta = \eta' \mathbf{B}\phi^r\,\mathbf{F}\eta = 0 \tag{16}$$

as $\phi^r\,(\mathbf{J}) = 0$. This contradicts (10). Hence they are linearly independent.

Let the space spanned by the vectors of (13) be denoted by $\mathbf{R}_1$ and $\mathbf{R}_2$ the space spanned by all the vectors which are conjugate to $\mathbf{R}_1$ w.r.t. $\mathbf{A}$ as well as $\mathbf{B}$; *i.e.*, those that satisfy the equations

$$\rho' \mathbf{B}\phi^q \mathbf{J}^p\eta = 0 \tag{17}$$

$$\rho' \mathbf{A}\phi^q \mathbf{J}^p\eta = 0 \tag{17'}$$

$$0 \leqslant p < m, \ 0 \leqslant q < r.$$

Since $\mathbf{A} = \mathbf{BJ}$ and $\phi^r\eta = 0$, (17') is not independent of (17); $\therefore$ there do exist $(n - mr)$ linearly independent vectors ρ which satisfy (17). We now show that *no vector of $\mathbf{R}_1$ satisfies the equations* (17); for, we must have, on the contrary, for some polynomials $f_0, f_1, \ldots f_{r-1}$, of degree $< m$, (in J).

$$\left\{ \overset{r}{\underset{0}{\Sigma}} f_t \, \phi^t \, \eta \right\}' \mathbf{B}\phi^q \mathbf{J}^p\eta = 0, \ \text{for } 0 \leqslant p < m, \ 0 \leqslant q < r, \tag{18}$$

which is the same as having

$$\eta' \mathbf{B}\phi^q \psi_1 \overset{r-1}{\underset{t=0}{\Sigma}} f_t \, \phi^t\eta = 0 \tag{18'}$$

for $0 \leqslant q < r$, and ψ_1 any arbitrary polynomial in J of degree $< m$. Let f_k be the first polynomial which is not zero among the f_t and ψ be so chosen as to satisfy (14). Putting $\psi_1 = \psi$ and $q = r - k - 1$ in (18') we obtain, after the vanishing terms are omitted

$$\eta' \mathbf{B}\phi^{r-1}\,\eta = 0$$

contradicting (10). Hence $\mathbf{R} = \mathbf{R}_1 + \mathbf{R}_2$ and if we choose the vectors of (13) and $(n - mr)$ linearly independent solutions ρ of the equations (17) as the co-ordinate vectors of $\mathbf{R}_n$ we have, from (3) and (17), the reduction

$$(\lambda \mathbf{A} + \mu \mathbf{B}) = (\lambda \mathbf{A}_1 + \mu \mathbf{B}_1) \dotplus (\lambda \mathbf{A}_1^* + \mu \mathbf{B}_1^*). \tag{19}$$

As $|\mathbf{B}| \neq 0$, $|\mathbf{B}_1| \neq 0$; if $\mathbf{J}_1 = \mathbf{B}_1^{-1}\mathbf{A}_1$ it follows from $\phi^r\,(\mathbf{J}) = 0$, as (19) is a direct resolution, that $\phi^r\,(\mathbf{J}_1) = 0$. It also easily follows that the

elementary divisors of $J_1 + tE$, where E is the unit matrix are $\phi^r(t)$, and unities only. Hence there cannot be any further similar reduction of J_1. This implies that $\lambda A_1 + \mu B_1$ is congruently irreducible.

We can obviously repeat this method to reduce $\lambda A_1^* + \mu B_1^*$ and we have therefore the following result:

THEOREM $1 \cdot 3 \cdot 2$.—Let B (or A) be non-singular. Then the pencil $\lambda A + \mu B$ is capable of being congruently reducible to the following direct sum

$$(\lambda A_1 + \mu B_1) \dotplus (\lambda A_2 + \mu B_2) \dotplus (\lambda A_3 + \mu B_3) \dotplus \ldots \dotplus (\lambda A_k + \mu B_k) \qquad (20)$$

where every component of (20) is irreducible. If $J_r = B_r^{-1} A_r$ then $J_r + tE$ has a single elementary divisor (apart from unities), which is an elementary divisor of $J + tE$. ($J = B^{-1}A$).

In a subsequent section we obtain simple canonical forms for these components by a more special choice of the co-ordinate-vectors of the carrier-space.

$1 \cdot 4$. We now consider the case $|A| = |B| = 0$. In this case the discriminant of the pencil

$$|\lambda A + \mu B| = \lambda^r \mu^s f(\lambda, \mu) \qquad (21)$$

where $f(\lambda, \mu)$ is divisible neither by λ nor by μ; $r, s > 0$. We assume that the order of the matrices is n and that for all pairs of lower order the decomposition of the following form holds

$$(\lambda A + \mu B) = (\lambda A_1 + \mu B_1) \dotplus (\lambda A_2 + \mu B_2) \dotplus (\lambda A_3 + \mu B_3) \qquad (22)$$

where $(\lambda A_1 + \mu B_1)$ is the component that corresponds to the factor λ^r; i.e., the component whose discriminant is λ^r (ignoring numerical factors); $(\lambda A_2 + \mu B_2)$ is the component that corresponds to μ^s and the other corresponds to $f(\lambda, \mu)$. It is clear then that A_1, B_2, A_3, B_3 are all non-singular. We now prove that the same decomposition holds for all pairs of order n also.

Proof.—The resolution of the form (22) holds trivially for pairs of order 1. As $|B| = 0$ there is a vector ξ_1 for which $B\xi_1 = 0$, choosing ξ_1 and $(n-1)$ other suitably chosen vectors ξ_2, ξ_3, $\ldots \xi_n$ as the co-ordinate-vectors of the carrier-space R_n, the pencil evidently assumes the following form:

$$\lambda A + \mu B = \begin{pmatrix} \lambda & \lambda & \lambda & \cdot & \cdot & \cdot & \cdot & \lambda \\ \lambda & & & & & & & \\ \lambda & & & & & & & \\ \cdot & & & & & & & \\ \cdot & & \lambda A_{n-1} + \mu B_{n-1} & & & & & \\ \cdot & & & & & & & \\ \cdot & & & & & & & \\ \lambda & & & & & & & \end{pmatrix} \tag{23}$$

where the various λ in the first-row-column of (23) represent several multiples of λ. (This notation is used throughout this proof for the sake of brevity.) We first of all observe that the transformations I_{rs} and T_{rs}, defined below are congruent and non-singular.

    $I_{rs} \rightarrow$ The interchange of the rth row with the sth followed by $\Big\}$ (24)
           the interchange of the same columns

    $T_{rs} \rightarrow$ Adding any multiple of the rth column to the sth $\Big\}$
           followed by the addition of the same multiple of the $\Big\}$ (25)
           rth row to the sth

    The desired decomposition is obtained by a succession of transformations I_{rs} and T_{rs}. Now, if the λ in the $(1, 1)$ place in (23) is not zero we apply a series of transformations of type T_{1r}, so as to make all other λ in the first row column zero. [This may alter $\lambda A_{n-1} + \mu B_{n-1}$ but we use the same notation for it for the sake of brevity.] Or

$$(\lambda A + \mu B) = (\lambda \ 1 + \mu \cdot 0) \dotplus (\lambda A_{n-1} + \mu B_{n-1}) \tag{26}$$

The discriminant of $(\lambda A_{n-1} + \mu B_{n-1})$ is $\lambda'^{-1}\mu' f(\lambda, \mu)$. Hence a decomposition of the form (22) holds for $(\lambda A_{n-1} + \mu B_{n-1})$. Combining the component with discriminant λ'^{-1} with $(\lambda \ 1 + \mu \ 0)$ we have a decomposition of the desired type for $(\lambda A + \mu B)$. If all the λ in the first row-column of (23) are zero the same result is evidently true. We therefore consider the case when the λ in the $(1, 1)$ place of (23) is zero and that one other λ in the first row-column does not vanish. By applying the transformation I_{1r}, if necessary, we can bring the non-vanishing λ to the $(2, 1)$ place and we therefore prove the result assuming that the λ in $(1, 2)$ place is not zero. We apply a series of transformations T_{2r} and make every other λ in the first row-column zero. Now the pencil is in the following form.

$$
\begin{pmatrix}
0 & \lambda & 0 & 0 & \cdot & \cdot & \cdot & 0 & 0 \\
\lambda & \lambda+\mu & \lambda+\mu & \lambda+\mu & \cdot & \cdot & \cdot & \lambda+\mu & \lambda+\mu \\
0 & \lambda+\mu & & & & & & & \\
0 & \lambda+\mu & & & & & & & \\
\cdot & \cdot & & & \lambda A_{n-2}+\mu B_{n-2} & & & & \\
\cdot & \cdot & & & & & & & \\
\cdot & \cdot & & & & & & & \\
0 & \lambda+\mu & & & & & & & \\
0 & \lambda+\mu & & & & & & &
\end{pmatrix} \qquad (27)
$$

where the λ, μ in the first and second row-columns stand for several
multiples of the same. Now

$$
| \lambda A + \mu B | = \lambda^2 | \lambda A_{n-2} + \mu B_{n-2} |
$$

$$
\therefore \quad | \lambda A_{n-2} + \mu B_{n-2} | = \lambda^{r-2}\mu^s f(\lambda, \mu). \qquad (28)
$$

Let

$$
(\lambda A_{n-2} + \mu B_{n-2}) = (\lambda A_r + \mu B_r) \; \dot{;} \; (\lambda A_s^* + \mu B_s^*) \qquad (29)
$$

where $| \lambda A_r + \mu B_r | = \mu^r$ and μ is not a factor of $| \lambda A_s^* + \mu B_s^* |$. We
transform B_r (which is non-singular and of rank s) to the diagonal form.
After this $(\lambda A + \mu B)$ assumes the following form:

$$
\begin{pmatrix}
0 & \lambda & 0 & 0 & \cdot & \cdot & \cdot & 0 & 0 & 0 & \cdot & 0 \\
\lambda & \lambda+\mu & \lambda+\mu & \cdot & \cdot & \cdot & \lambda+\mu & \lambda+\mu & \lambda+\mu & \lambda+\mu & \cdot & \lambda+\mu \\
0 & \lambda+\mu & \lambda+\mu & \lambda & \lambda & & \lambda & \lambda & 0 & 0 & \cdot & 0 \\
0 & \cdot & \lambda & \lambda+\mu & \lambda & \cdot & \lambda & \lambda & 0 & & & \cdot \\
\cdot & & \lambda & \lambda & \lambda+\mu & \cdot & \cdot & \lambda & \cdot & & & \\
\cdot & & & & & & & & & & & \\
0 & \lambda+\mu & \lambda & \cdot & & & & & & & & \\
0 & \lambda+\mu & \lambda & \lambda & \cdot & \cdot & \lambda & \lambda+\mu & 0 & 0 & \cdot & 0 \\
0 & \lambda+\mu & 0 & 0 & \cdot & \cdot & 0 & 0 & & & & \\
\cdot & \cdot & \cdot & & & & & & & & & \\
\cdot & \cdot & \cdot & & & & & & \lambda A_s^* + \mu B_s^* & & & \\
\cdot & \cdot & \cdot & & & & & & & & & \\
0 & \lambda+\mu & 0 & 0 & \cdot & \cdot & 0 & 0 & & & &
\end{pmatrix} \qquad (30)
$$

where we write λ and μ at the various places for various multiples of the same as we did before. As B_s is of rank s the μ in the (3, 3), (4, 4),... $(s+2, s+2)$ places in (30) are not zero. Apply transformations of type T_{r2}, $3 \leqslant r \leqslant s+2$, so that the μ in the second row which are in the (2, k), $[2 < k \leqslant s+2]$ places become zero. (The corresponding elements of the second column also become zero.) The λ in the same places are made to vanish by a succession of transformations of type T_{1r}, $3 \leqslant r \leqslant s+2$; then $\lambda A_r + \mu B_r$ becomes a component of $(\lambda A + \mu B)$ itself and we have

$$(\lambda A + \mu B) = (\lambda A_r + \mu B_r) \dotplus (\lambda C + \mu D) \qquad (31)$$

where $|\lambda A_r + \mu B_r| = \mu^r$ and $\therefore |\lambda C + \mu D| = \lambda^r f(\lambda, \mu)$. As $|C| \neq 0$ we have the further decomposition

$$(\lambda C + \mu D) = (\lambda P + \mu Q) \dotplus (\lambda X + \mu Y) \qquad (32)$$

where $|\lambda P + \mu Q| = \lambda^r$ and $|\lambda X + \mu Y| = f(\lambda, \mu)$. Substituting this in (31) we have the desired type of decomposition (22). Hence even when $|A| = |B| = 0$, a decomposition of form (20) holds for any non-singular pencil as we can congruently reduce the components in (22) into irreducible components by employing Theorem 1·3·1 as one of the three components is certainly non-singular.

§2. CANONICAL FORMS OF AN IRREDUCIBLE COMPONENT

2·1. Let us take an irreducible component of (20), $\lambda A_1 + \mu B_1$; at least one of the matrices A_1 or B_1 is non-singular. Let us take for definiteness that $|B_1| \neq 0$. Then $J_1 + tE$, where $J_1 = B_1^{-1}A_1$ has the single elementary divisor $\phi^r(t)$ apart from unities, where

$$\phi(t) = t^m - a_{m-1} t^{m-1} - a_{m-2} t^{m-2} - \cdots - a_0 \qquad (33)$$

is an irreducible polynomial. Let us first take the case of a simple elementary divisor, *i.e.*, $r=1$. We choose the co-ordinate vectors to be those in (12) in the following order:

$$\eta, J_1\eta, J_1^2\eta, \cdots J_1^{m-1}\eta \qquad (34)$$

Then A_1 and B_1 assume the canonical forms I_1 and I_0 whose elements are calculated by employing (3), *i.e.*, if $I_0 = |i_{rs}^0|$, and $I_1 = |i_{rs}^1|$ we have

$$i_{rs}^0 = (J_1{}^r\eta)' B_1 J_1{}^s\eta = \eta' B_1 J_1{}^{r+s}\eta \qquad (35)$$

as $B_1 J_1{}^s$ is symmetric. Hence we can write

$$i_{rs}^0 = i_{r+s}, \quad i_{rs}^1 = i_{r+s+1}, \qquad (36)$$

as $A_1 = B_1 J$. From $\phi(J_1) = 0$, it follows from (35) and (36) that i_r satisfies the recurrence equation generated by $\phi(t)$, *i.e.*,

$$i_{r+m} = a_0 i_r + a_1 i_{r+1} + \cdots a_{m-1} i_{r+m-1} \qquad (37)$$

for every $r > 0$. The canonical forms are therefore

$$I_0 = |i_{i+r}|, \quad I_1 = |i_{r+k+1}| \tag{38}$$

where the i_t satisfy (37) We say that these canonical forms are generated by the initial co-ordinate vector η of (34) or it is generated by

$$[i_0, i_1, \ldots i_{m-1}] \tag{39}$$

as these m numbers along with ϕ determine the canonical forms

2·2. We now take up the case $r > 1$. Taking the co-ordinate vectors to be $J_1'\eta$, $0 \leqslant t < mr$, we obtain a form analogous to (38). These forms depend on mr initial constants and do not exhibit clearly the fact that the corresponding elementary divisor is the power of an irreducible polynomial. We proceed to obtain forms which depend only on m initial constants. Let us take the co-ordinate vectors to be those of (12) in the following order:

$$\eta, J_1 \eta, J_1' \eta, \ldots J_1^{m-1} \eta, \phi \eta, \phi J_1 \eta, \ldots \phi J_1^{m-1} \eta, \phi^k \eta, \ldots \phi^{r-1} J_1^{m-1} \eta \tag{40}$$

[we write ϕ for $\phi(J_1)$]. We obtain the following form for B_1 (and a similar form for A_1):

$$B_1 \rightarrow
\begin{pmatrix}
B^0 & B^1 & B^2 & \cdot & \cdot & \cdot & B^{r-1} \\
B^1 & B^2 & \cdot & \cdot & \cdot & B^{r-1} & 0 \\
B^2 & B^3 & \cdot & B^{r-1} & \cdot & 0 & 0 \\
\cdot & & & & & & \\
\cdot & & & & & & \\
\cdot & B^{r-1} & \cdot & \cdot & \cdot & \cdot & 0 \\
B^{r-1} & 0 & \cdot & \cdot & \cdot & \cdot & 0
\end{pmatrix} \tag{41}$$

[As $\phi^r \eta = 0$ all the elements below the principal diagonal are zero] where B^λ are matrices of order m whose elements are given by

$$b^\lambda{}_{pq} = \eta' B_1 \phi^\lambda J_1^{p+q} \eta \tag{42}$$

$$0 \leqslant \lambda < r, \quad 0 \leqslant p, \ q < m.$$

The B^λ are matrices of the same type as in (38) with no recurrence relation among their coefficients except when $\lambda = (r - 1)$ in which case we write

$$b_{pq}{}^{r-1} = i_{p+q} \tag{43}$$

and it is clear that i_t satisfy the recurrence relation determined by ϕ. From (42) we see that the matrices are known completely if the first row (or column) elements of $B^0, B^1, \cdots B^{r-1}$ are known; all the other coefficients

can be calculated from them as expressions involving the coefficients of ϕ. We now prove

THEOREM 2·2·1.—It is possible to choose the co-ordinate vectors of the carrier space so that the first row elements of B^t, $0 \leqslant t < r - 1$ of (40) are equal to any $m(r-1)$ arbitrarily given quantities. Hence the components corresponding to the same elementary divisor and having the matrix blocks corresponding to B^{r-1} identical are necessarily congruent.

Proof.—We show that this can be obtained by replacing η by ρ (where ρ is a suitably chosen initial vector) in (40) and taking the co-ordinate vectors to be as given there Let us put

$$\rho = \sum_{k=0}^{(r-1)} f_k \ \phi^k \ \eta \tag{44}$$

where the f_k are polynomials in J_1, of degree $< m$, which are to be determined. Let $f_0 \neq 0$ be fixed arbitrarily in advance We prove by induction that the other f_k can be chosen so that the first row elements of B^t, $0 \leqslant p < (r-1)$ are equal to the given quantities. We assume that $f_1, f_2, f_3, \ldots f_t$ are chosen so that

$$b_{0\rho}{}^k, \text{ for } r - 1 > k > r - t - 1, \ 0 \leqslant p < m$$

are equal to the given quantities. As $\phi' \eta = 0$, it is easily seen that

$$b_{0\rho}{}^{r-3-t} = \eta' \ B_1 \ \phi^{r-3-t} \ J_1{}^p \ (f_0 + f_1\phi + \ldots f_{t+1}\phi^{t+1})^s \ \eta. \tag{45}$$

As the characteristic of the field is not 2, we can write (45) as

$$2\eta' B_1 f_0 f_{t+1}\phi^{r-1} \ J_1{}^p \ \eta = b_{0\rho}{}^{r-2-t} + x_\rho, \ 0 \leqslant p < m \tag{46}$$

where x_ρ is a quantity which is already determined. Let

$$f_{t+1} = \sum_{v=0}^{m-1} p_v \ J_1{}^v.$$

Then (46) is a set of m linear non-homogeneous equations in the p_v. Hence it is possible to determine p_v, f_{t+1} so that the equation (46) is satisfied with the given values for the $b_{0\rho}{}^{r-2-t}$; for, if it is not so there must be a set of values p_v or f_{t+1} which satisfy the corresponding set of homogeneous equations, *i.e.*, there exists an $f_{t+1} \neq 0$, of degree $< m$ which satisfies the equation

$$\eta' B_1 f_0 f_{t+1} \ \phi^{r-1} \ J_1{}^p \ \eta = 0, \text{ for } 0 \leqslant p < m \tag{47}$$

$\therefore$ for every polynomial ψ of degree $< m$

$$\eta' \ B_1 \ \phi_0 \ \psi \ \phi^{r-1} \eta = 0, \tag{48}$$

where $\phi_0 = f_0 f_{t+1} \pmod \phi$ is a non-vanishing polynomial of degree $< m$ since ϕ is irreducible and f_0, f_{t+1} are non-vanishing polynomials of degree

$< $(that of $\phi = m$). Choose ψ so that

$$\phi_0 \psi \equiv 1 \;(\mathrm{mod}\; \phi)$$

We then obtain

$$\eta' \, B_1 \, \phi^{r-1} \, \eta = 0. \tag{49}$$

This contradicts the fundamental condition (10). Hence j_{t+1} can be chosen so that the $b_{0\rho}^{r-t-t'}$ are equal to the previously assigned quantities. f_1 can be chosen initially so that $b_{0\rho}^{r-2}$ are equal to the previously assigned quantities as f_0 is known. Hence the result is true.

2·3. The best canonical forms are obtained if we put $b_{0\rho}^{\lambda} = 0$, for $0 \leqslant p < m$, $0 \leqslant \lambda < r$. Utilising the equations (41) we can obtain the other elements of B_1 and also of A_1. Writing $b_{0\rho}^{r-1} = i_{\rho+\rho'}$ we obtain the following canonical form for $\lambda A_1 + \mu B_1$:

$$
\begin{pmatrix}
0 & 0 & 0 & \cdot & \cdot & \cdot & \cdot & P, & I \\
0 & 0 & 0 & \cdot & \cdot & P, & I & 0 \\
0 & 0 & 0 & 0 & 0 & P, & I & 0 & 0 \\
 & \cdot & \cdot & \cdot & & & & & \\
 & & & & & & & & \\
 & \cdot & & & & & & & \\
\cdot & P, & I & \cdot & \cdot & \cdot & & & 0 \\
P, & I & 0 & \cdot & \cdot & \cdot & \cdot & & 0 \\
I & 0 & 0 & \cdot & \cdot & \cdot & \cdot & & 0
\end{pmatrix}
\tag{50}
$$

where $I = \lambda I^1 + \mu I^0$, with I^0 and I^1 are matrices of the same form as in (38) [when we put $f_0 = 1$, in (44) the i, will be identical with those given by (43)] and $P = \lambda X^1 + \mu X^0$, where

$$
X^0 =
\begin{pmatrix}
0 & 0 & 0 & 0 & \cdot & \cdot & 0 & 0 \\
0 & 0 & 0 & \cdot & \cdot & \cdot & 0 & x_0 \\
0 & 0 & \cdot & \cdot & \cdot & 0 & x_0 & x_1 \\
0 & 0 & \cdot & \cdot & x_0 & x_1 & x_2 \\
\cdot & & & & & & & \\
& & & & & & & \\
0 & 0 & x_0 & x_1 & \cdot & \cdot & \cdot & x_{m-2} \\
0 & x_0 & x_1 & x_2 & \cdot & \cdot & \cdot & x_{m-2}
\end{pmatrix}
\qquad
X^1 =
\begin{pmatrix}
0 & 0 & \cdot & \cdot & \cdot & 0 & x_0 \\
0 & 0 & \cdot & \cdot & \cdot & x_0 & x_1 \\
0 & 0 & \cdot & \cdot & x_0 & x_1 & x_2 \\
\cdot & & & & & & \\
& & & & & & \\
0 & x_0 & x_1 & \cdot & \cdot & \cdot & x_{m-2} \\
x_0 & x_1 & x_2 & \cdot & \cdot & \cdot & x_{m-1}
\end{pmatrix}
\tag{51}
$$

The x_ρ are calculated by means of the following recurrence formula

$$x_\rho = i_\rho + \sum_{t=0}^{\rho-1} a_{m-\rho+t} \, x_t, \quad 0 \leqslant p < m, \tag{52}$$

where $i_\rho = \rho' B_1 \phi^{r-1} J_1{}^\rho \rho$ and a_t are the coefficients of $\phi(t)$. These canonical forms (50) can be looked upon as a generalisation of the Weierstrassian canonical forms which correspond to the case when ϕ is of degree 1.

Definition 2·2·1.—We call the canonical forms (50) [or (41)] the forms generated by the initial co-ordinate vector ρ [or η] or as those generated by $(i_0, i_1, i_2, \cdots i_{m-1})$.

Canonical forms for an irreducible component in which $|B_1| = 0$, $\therefore |A_1| \neq 0$, are obtained from these with an interchange of A and B.

§ 3. SOME APPLICATIONS OF THE CANONICAL FORMS OF § 2

3·1. If $\lambda A + \mu B$ is a pencil in the real-number field and if the quadratic form corresponding to one of the (symmetric) matrices is +ve definite, we have then the classical result that the elementary divisors of the pencil are all simple (and linear also). We proceed to obtain analogous results valid for any field of characteristic other than 2. The notion of definiteness cannot be introduced in the case of an arbitrary field which is not ordered. We replace the condition that—*the quadratic form is definite by*—*the quadratic form is not capable of assuming all values*, and obtain corresponding theorems valid for any field.

3·2. Let the pencil of two symmetric matrices $(\lambda A + \mu B)$ have an irreducible component $(\lambda A_1 + \mu B_1)$, $|B_1| \neq 0$, where the minimum-polynomial of $J_1 = B_1{}^{-1} A_1$ is ϕ^r where ϕ is an irreducible polynomial of degree m. Then the pencil $(\lambda A + \mu B)$ has an elementary divisor which is the rth power of an irreducible homogeneous polynomial in (λ, μ) of degree m—i.e., *it has an elementary divisor which is not simple* From Theorem 3·2·1 it follows that there is a vector ρ for which

$$\rho' B_1 \phi^s J_1{}^t \rho, \quad 0 \leqslant s < r-1, \ 0 \leqslant t < m, \tag{53}$$

$[\phi(J_1) = \phi]$ are equal to any $m(r-1)$ previously assigned quantities; or, in other words, the quadratic forms represented by the symmetric matrices $B_1 \phi^s J_1{}^t$ are capable of assuming simultaneously for some vector ρ any arbitrarily assigned values. We can replace the quadratic forms in (53) by those that correspond to

$$B_1 J_1{}^t, \quad 0 \leqslant t \leqslant m(r-1). \tag{54}$$

If $m(r-1) > 1$, this set of quadratic forms includes that which corresponds to $A_1 = B_1 J_1$. Therefore we obtain, in particular that the quadratic forms

A5

corresponding to A_1, B_1, and *a-fortiori* the quadratic forms corresponding to A and B are capable of assuming simultaneously any two arbitrarily assigned values The same result is true when $|\ B_1\ | = 0$, and $|\ A_1\ | \neq 0$. Representing the quadratic forms corresponding to a matrix C by C itself we obtain the following theorems:

THEOREM 3·2 1. Let the pencil of quadratic forms $(\lambda A + \mu B)$ have an elementary divisor ϕ^r, where $r > 1$, and ϕ an irreducible homogeneous polynomial of degree m in λ, μ If $m\ (r-1) > 1$, the quadratic forms A and B are capable of assuming *simultaneously* any two arbitrarily assigned values, the field of coefficients being any arbitrary one characteristic $\neq 2$.

THEOREM 3·2·2.—Let the assumptions of 3 2·1 hold and in addition let $|\ B\ | \neq 0$ and $\phi \neq \lambda$ Then the quadratic forms BJ^t, $0 \leqslant t \leqslant m\ (r-1)$ are capable of assuming *simultaneously* any arbitrarily assigned values.

3 3. Let us now consider the case $m = 1$, $r = 2$, *i.e*, the elementary divisor is $(p\lambda + q\mu)^2$ If $pq \neq 0$, then the quadratic form A is capable of assuming every value; and the same is true of B also. In case the elementary divisor is λ^2 (or μ^2) we can only say that A (or B) is capable of assuming all values. Hence we have the following theorems:

THEOREM 3·3·1.—Let the pencil $\lambda A + \mu B$ have an elementary divisor $(p\lambda + q\mu)^2$, $pq \neq 0$; then the quadratic form A is capable of assuming every value and the same is true of B. If the elementary divisor is either λ^2 or μ^2 then either the quadratic form A or the quadratic form B is capable of assuming every value

THEOREM 3 3·2.—Let the quadratic forms A and B be incapable of assuming each one of some two given values respectively; then the pencil has only simple elementary divisors (not necessarily linear).

3 4. In the case of the real-number-field, if a quadratic form is not capable of assuming a certain value then it must be ±ve definite or semi-definite; and the elementary divisors are powers of linear or quadratic polynomials in (λ, μ) When an elementary divisor which is an irreducible quadratic exists, one can prove easily from the canonical form that the quadratic forms are capable of assuming *simultaneously* any two given values. As particular cases of theorems in 3·2 and 3·3 we have

THEOREM 3·4·1.—Let $\lambda A + \mu B$ be a pencil of quadratic forms in the real number field. Let B be ±ve *semi*-definite. Then the discriminant of the pencil has only real roots.

THEOREM 3 4·2.—Let $\lambda A + \mu B$ be a pencil in which both the quadratic forms A and B are ±ve semi-definite. Then the elementary divisors of the

pencil are all linear and hence we can simultaneously transform them to sums of squares.

§ 4. CRITERIA FOR THE CONGRUENCE OF TWO SYM-SYM PAIRS

4·1. We proceed to obtain the criteria for the congruence of two sym-sym pairs $\lambda A + \mu B$ and $\lambda A^* + \mu B^*$. A known necessary condition is that they have identical elementary divisors. We assume that this is always satisfied. If the pairs are congruent, then it must be possible to choose n linearly independent vectors in the carrier-space R_n so that

$$(\lambda a_{rs}^* + \mu b_{rs}^*) = \xi_r' (\lambda A + \mu B) \, \xi_s. \tag{55}$$

Following the method of paragraph (1·4) we can congruently transform the pairs into direct sums

$$(\lambda A + \mu B) = (\lambda A_1 + \mu B_1) \dotplus (\lambda A_2 + \mu B_2) \tag{56}$$

(with a similar decomposition for the starred pair), where the determinants

$$|\,\lambda A_1 + \mu B_1\,| = |\,\lambda A_1^* + \mu B_1^*\,| = \lambda^\rho \tag{57}$$

and $|\,\lambda A_2 + \mu B_2\,| = |\,\lambda A_2^* + \mu B_2^*\,|$ is not divisible by λ (constant factors if any are ignored). We now prove the following result·

THEOREM 4·1·1.—Let $(\lambda A + \mu B)$ be congruent to $(\lambda A^* + \mu B^*)$, then, with the direct-sum decomposition (56), the two components on the R.H.S. of (56) are congruent to the corresponding *starred* pairs.

Proof.—Let R_1 and R_2 be the sub-spaces of the carrier-space that correspond to $(\lambda A_1 + \mu B_1)$ and $(\lambda A_2 + \mu B_2)$ respectively; and the same starred represent these sub-spaces that correspond to the respective starred components. Let us represent the vectors of these sub-spaces by ξ_1, ξ_2, ξ_1^*, ξ_2^* respectively. We take the starred pencil as having been obtained from the other by means of transformation of co-ordinates of the carrier-space. The theorem is proved if we show that ξ_1 (or ξ_2) can only be transformed to a ξ_1^* (or ξ_2^*) by this mapping. Now from the assumptions of the decomposition (56), it is clear that A_1, A_1^*, B_2, B_2^* are all non-singular; and any vector ξ_1 of R_1 has the following property [on account (57)]

$$(A_1^{-1}B_1)^\ell \, \xi_1 = 0 \tag{58}$$

Putting $(A_1^{-1}B_1)^k \, \xi_1 = \xi_1^k$, we obtain · ξ_1^k always belongs to R_1 and satisfies the equations

$$A_1\xi_1^k = B_1\xi_1^{k-1}, \quad \therefore \; A\xi_1^k = B\xi_1^{k-1}, \; \xi_1^\rho = 0 \tag{59}$$

or given any vector $\xi_1 = \xi_1^0$ of R_1 the following chain of linear equations

$$A\xi_1^1 = B\xi_1^0, \; A\xi_1^2 = B\xi_1^1, \cdots A\xi_1^{k-1} = B\xi_1^{k-1}, \; A\xi_1^\rho = B\xi_1^{\rho-1} \tag{60}$$

can be solved successively for $\xi_1{}^k$; and $\xi_1{}^0 = 0$. The same property is true for vectors of $R_1{}^*$ also. For a vector $\xi_2 = \xi_2{}^0$ of R_2 we similarly obtain that the chain of equations

$$B\xi_2{}^1 = A\xi_2{}^0,\ B\xi_2{}^2 = A\xi_2{}^1,\cdots B\xi_2{}^{k+1} = A\xi_2{}^k,\cdots \qquad (61)$$

can be solved indefinitely. The same is true of the vectors of $R_2{}^*$ also.

We now prove that a vector of R_1 can only be transformed to a vector of $R_1{}^*$ by the congruent transformation. For, suppose on the contrary that a vector ξ_1 of R_1 is transformed into a $\xi_1{}^* + \xi_2{}^*$. Now the chain of equations of type (59) are satisfied by ξ_1 as well as $\xi_1{}^*$. As a congruent transformation retains equations of form (59) and (60), we obtain that a chain of equations of the form (60) can be solved starting with the initial vector $\xi_2{}^*$ of $R_2{}^*$ instead of $\xi_1{}^0$. Writing $\xi_2{}^* = \eta^0$, we obtain that the chain of equations

$$A\eta^1 = B\eta^0,\ A\eta^2 = B\eta^1,\cdots A\eta^k = B\eta^{k-1} \qquad (60')$$

can be solved successively for the η^k with $\eta^0 = 0$. Let ρ^k be the components of η^k in $R_2{}^*$; then $\eta^0 = \rho^0$ as $\eta^0 = \xi_2{}^*$ is in $R_2{}^*$ and we deduce from (60') that the chain of equations

$$A_2{}^*\rho^k = B_2{}^*\rho^{k-1},\ \rho^0 = 0.$$

As $|B_2{}^*| \neq 0$, we obtain that

$$\eta^0 = \xi_2{}^* = \rho^0 = [(B_2{}^*)^{-1}\,A_2{}^*]^0\,\rho^0 = 0$$

or the vectors of R_1 are transformed to vectors $R_1{}^*$ only. Now let a vector ξ_2 of R_2 be transformed to $\xi_1{}^* + \xi_2{}^*$ (where $\xi_1{}^*$ belongs to $R_1{}^*$ and $\xi_2{}^*$ belongs to $R_2{}^*$). We then obtain that the vector $\xi_1{}^*$ satisfies an equation of the form (61); i.e., writing $\xi_1{}^* = \eta^0$ we obtain that the following chain of equations can be solved indefinitely for the successive η^k

$$B\eta^{k+1} = A\eta^k \qquad (61')$$

Let ρ^k be the components of η^k in the sub-space $R_1{}^*$, then $\rho^0 = \eta^0 = \xi_1{}^*$ and from (61') we deduce that the following set of equations

$$B_1{}^*\rho^{k+1} = A_1{}^*\rho^k \qquad (61'')$$

can be solved successively for the ρ^k. As $A_1{}^*$ is non-singular we obtain that

$$\xi_1{}^* = \rho_0 = [(A_1{}^*)^{-1}\,B_1{}^*]^l\,\rho^0 = 0$$

or the vectors of R_2 are transformed to those of $R_2{}^*$ only.

4·2. We therefore proceed to obtain the additional criteria for the congruence of $(\lambda A^* + \mu B^*)$ and $(\lambda A + \mu B)$ where these have identical

elementary divisors and that B and B* are non-singular. The case when A and A* are non-singular can be treated in exactly the same way and on account of theorem $(4\cdot1\cdot1)$ the problem of congruence can be reduced to these two cases always. Let $J = B^{-1}A$ and let its minimum-polynomial $F = F(J)$ be split up into relatively prime factors

$$\phi_1 \cdot \phi_2 \ldots \phi_k. \tag{62}$$

Following the procedure of § 1 we decompose $(\lambda A + \mu B)$ into

$$(\lambda A + \mu B) = (\lambda A_1 + \mu B_1) \dotplus (\lambda A_2 + \mu B_2) \dotplus \ldots \dotplus (\lambda A_k + \mu B_k) \tag{63}$$

where $\lambda A_\rho + \mu B_\rho$ is the direct sum of all irreducible components which correspond to those elementary divisors which are factors of ϕ_ρ; the *starred* pair also has a similar decomposition. Then we have the following theorem:

THEOREM $4\cdot2\cdot1$.—With the decomposition (63) the components $(\lambda A_\rho + \mu B_\rho)$ must be congruent to the components $(\lambda A_\rho^* + \mu B_\rho^*)$ respectively.

Proof.—Let the decomposition of the carrier-space R^n corresponding to the direct decomposition (63) be

$$R_n = R_1 + R_2 + \ldots + R_k = R_1^* + \ldots + R_k^*. \tag{64}$$

Let the vectors of R_ℓ, R_ℓ^* be represented by ξ_ℓ, ξ_ℓ^*, etc. A vector ξ_ℓ of R_ℓ satisfies the equation (as well as any ξ_ℓ^* of R_ℓ^*)

$$\phi_\ell (B_\ell^{-1} A_\ell) \xi_\ell = 0, \quad \therefore \phi_\ell (J) \xi_\ell = 0 \tag{65}$$

where $J = B^{-1}A$. For the sake of brevity we write f for $f(J)$ in the sequel Now suppose a vector ξ_1 of R_1 is transformed to $\xi_1^* + \xi^*$ where ξ_1^* belongs to R_1^* and ξ^* belongs to $R_2^* + R_3^* + \ldots + R_k^*$. We prove that $\xi^* = 0$. For,

$$\phi_1 (J) \xi^* = \phi_1 [\xi_1 - \xi_1^*] = 0, \text{ and } \psi \xi^* = \phi_2 \phi_3 \ldots \phi_k \, \xi^* = 0 \tag{66}$$

As ϕ_1 and ψ are relatively prime we can find polynomials f_1 and f_2 so that $(f_1\phi_1 + f_2\psi) = 1$. Hence we obtain from (66)

$$\xi^* = (f_1\phi_1 + f_2\psi) \, \xi^* = 0. \tag{67}$$

Hence the vectors of R_ℓ are transformed to those of R_ℓ^* and *vice versa* We have proved therefore the desired result.

4·3. Hence we need only obtain the criteria for the congruence of the pairs $(\lambda A + \mu B)$, $(\lambda A^* + \mu B^*)$, where these have identical elementary divisors which are all powers of the same irreducible polynomial. Let us assume that the two pairs are in the completely reduced form, *i.e.*,

$$(\lambda A + \mu B) = (\lambda A_1 + \mu B_1) \dotplus (\lambda A_2 + \mu B_2) \dotplus (\lambda A_3 + \mu B_3) \dotplus \ldots \dotplus (\lambda A_k + \mu B_k) \tag{68}$$

where the components on the R.H.S. of (68) are all irreducible, with a similar decomposition for the other pair. Among these let there be n_1 components corresponding to the elementary divisors ϕ^{r_1}, n_2 components to elementary divisors ϕ^{r_2}, ... n_p components to elementary divisors ϕ^{r_p}, where $\phi(t) = t^m$ $-\sum\limits_{0}^{m-1} a_\nu t^\nu$ is an irreducible polynomial in t of degree m and $r_1 > r_2 > \ldots > r_p$. We know that each one of these irreducible components is known as soon as the initial co-ordinate vector of each component is known. Let $\mathbf{J} = \mathbf{B}^{-1}\mathbf{A}$. Let the initial co-ordinate vectors of these irreducible components be, in order,

$$\xi_{sq_s}, \quad 1 \leqslant s \leqslant p, \; 1 \leqslant q_s \leqslant n_s. \tag{69}$$

Let these *starred* represent the corresponding quantities of the congruent pencil $\lambda \mathbf{A}^* + \mu \mathbf{B}^*$. It is easy to see that the transformation carrying one pair to the other is determined if we know the transformation of the initial co-ordinate vectors. We therefore write below the transformation of the initial co-ordinate vectors of the various irreducible components:

$$\xi_{tq_t}{}^* = \sum_{l=1}^{p} \sum_{s_l=1}^{n_l} \mathbf{T}_{q_l}{}^{tls_l} \xi_{ls_l} \tag{70}$$

$$1 \leqslant q_t \leqslant n_t, \; 1 \leqslant t \leqslant p;$$

where, on account of $\phi^{r_k}(\mathbf{J}) \, \xi_{kq_k}{}^* = 0$,

$$\text{for } t > v, \qquad \mathbf{T}_{q_l}{}^{tvs} = \sum_{u=0}^{r_t-1} \mathbf{T}_{q_\mu}{}^{tvs} \phi^{u+r_s-r_t}$$

$$\left.\begin{array}{c}\\ \\ \\ \end{array}\right\} \tag{71}$$

$$\text{and for } t < v, \qquad \mathbf{T}_{q_l}{}^{tvs} = \sum_{u=0}^{r_s-1} \mathbf{T}_{q_\mu}{}^{tvs} \phi^{u},$$

the $\mathbf{T}_{lu}{}^{ijk}$ being polynomials in $\mathbf{J}$ of degree $< m$.

We assume that the components in (68) are in the canonical forms (41). Then the following conditions must be *necessary*:

$$\xi_{tq_t}{}^{*\prime} \, \mathbf{B} \phi^{r-1} \, \mathbf{J}^s \, \xi_{tq_t'}{}^* = i_{q_t q_t'} \, \delta_{q_t q_t'}, \; 0 \leqslant s < m, \tag{72}$$

where the component whose initial vector is $\xi_{tq_t}{}^*$ is generated by $(i_{q_t 0}{}^*, i_{q_t 1}{}^*, \cdots i_{q_t(m-1)}{}^*)$. [*Cf* Definition 2·2·1.] Substituting the values for ξ^* from (70), we obtain

$$\sum_{s=1}^{n_t} \xi_{ts}{}' \mathbf{B} \mathbf{T}_{q_t 0}{}^{tts} \mathbf{T}_{q_t' 0}{}^{tts} \phi^{r-1} \, \mathbf{J}^l \, \xi_{ts} = \delta_{q_t q_t'} \, i_{ql}{}^* \tag{73}$$

$$1 \leqslant t \leqslant p, \; 0 \leqslant l < m, \; 1 \leqslant q_t, \; q_t' \leqslant n_t.$$

[Since $\xi_{l_i}{}'B\phi^i I^l \xi_{r_i} = 0$, for $r \neq l$, as ξ_{l_i} and ξ_{r_i} are initial vectors of different irreducible components, and $\phi^i \xi_{l_i} = 0$, for $i > l$, all other terms drop out], *i.e.*, the existence of the polynomials

$$T_{q_l0}{}'{}^{tz}, \quad 1 \leqslant q_l, \; q_l' \leqslant n_l, \; 1 \leqslant t \leqslant p.$$

satisfying (73) is necessary for the congruence of the given pairs. We transform these fundamental criteria into more elegant forms in the next paragraph.

4·4. We take a fixed t and write for brevity ξ_{l_i} as ξ_i, $T_{q_l0}{}'{}^{tz}$ as $T_{q0}{}'$, r_t as r and n_t as n. For this fixed t, the concerned equations in (73) may be written, with the present notation:

$$\sum_{r=1}^{n} \xi_s{}' BT_{q_0}{}'{}^s T_{v_0}{}^s \phi^{l-1} J^l \xi_z = \delta_{qv} i_{ql}{}^* \tag{74}$$

$$1 \leqslant q, \; v \leqslant n, \; 0 \leqslant l < m$$

$T_{q0}{}'$ are polynomials in J of degree $< m$ $i_{ql}{}^*$, i_{ql}, are defined for all l by the recurrence relation generated by the polynomial ϕ; then (74) holds for all l as $\phi^r (J) \xi_z = 0$. Let $I_{q_0} = |i_{ql,l+n}|$, [*cf* (38)], with $I_{q_0}{}^*$ defined similarly, $0 \leqslant l$, $u < m$. Let

$$T_{q0}{}''T_{v0}{}' = P_{qv}{}' \; [\text{mod } \phi] \tag{75}$$

$$P_{qv}{}' = \sum_{u=0}^{m-1} p_{qvu}{}' J^u \tag{76}$$

Substituting in (74) we obtain:

$$\sum_{u=0}^{m-1} \sum_{s=1}^{n} p_{qvu}{}' \xi_s{}' B\phi^{r-1} J^{u+l} \xi_z = \delta_{qv} i_{ql}{}^*$$

or

$$\sum_{u=0}^{m-1} \sum_{s=1}^{n} p_{qvu}{}' i_{s,u+l} = \delta_{qv} i_{ql}{}^* \tag{77}$$

Let H be the companion matrix corresponding to the polynomial ϕ, *i.e.*,

$$H = \begin{pmatrix} 0 & 1 & 0 & 0 & \cdot & \cdot & 0 \\ 0 & 0 & 1 & 0 & \cdot & \cdot & 0 \\ \cdot & \cdot & & & \cdot & \cdot & \cdot \\ \cdot & & & & & & \cdot \\ 0 & 0 & \cdot & & \cdot & 0 & 1 \\ a_0 & a_1 & \cdot & \cdot & \cdot & \cdot & a_{m-1} \end{pmatrix} \tag{78}$$

so that ϕ (H) = 0; let $\tau_q{}^s = \mathrm{T}_q{}^r$ (H), $\pi_{qv}{}^s = \sum\limits_{u=0}^{m-1} p_{qvu}{}^s \mathrm{H}^u$.   From (75) and (76) we obtain

$$\tau_q{}^s \tau_v{}^s = \pi_{qv}{}^s \tag{79}$$

and (77) can be written:

$$\sum\limits_{s=1}^{n} \tau_q{}^s \tau_v{}^s \mathrm{I}_{r0} = \delta_{qv} \mathrm{I}_{q0}^*. \tag{80}$$

It is readily verified that if $\mathrm{G} = |\,g_{u+l}\,|$ is a matrix of the same form as I_{r0} with the same recurrence equation for its elements, $\mathrm{GI}_{r0}{}^{-1}$ is a polynomial in H of degree $< m$. I_{r0} is non-singular as B is assumed to be non-singular [cf. (50)]   Hence (80) can be written as

$$\sum\limits_{s=1}^{n} \tau_q{}^s \tau_v{}^s (\mathrm{I}_{r0} \mathrm{I}_{10}{}^{-1}) = \delta_{qv} (\mathrm{I}_{q0}^* \mathrm{I}_{10}{}^{-1})$$

writing $\mathrm{I}_{r0}\mathrm{I}_{10}{}^{-1} = \rho_s$ (H) = ρ_s, $\mathrm{I}_{s0}^*\mathrm{I}_{10}{}^{-1} = \rho_s^*$ (H) = ρ_s^* this takes the form:

$$\sum\limits_{s=1}^{n} \tau_q{}^s \tau_v{}^s \rho_s = \delta_{qv} \rho_s^* \tag{81}$$

Now the $\tau_q{}^s$, $\rho_s, \ldots$ may be taken as numbers of the algebraic field K (θ), where ϕ (θ) = 0   Then the condition (81) is equivalent to the following.—

In K (θ) the diagonal matrices $\rho_1 \dotplus \rho_2 \dotplus \cdots \dotplus \rho_n$, $\rho_1^* \dotplus \rho_2^* \dotplus \cdots \dotplus \rho_n^*$ are congruent. $\left.\right\}$ (82)

Hence the necessary criteria for the congruence of two pairs are a number of conditions of type (82), apart from the identity of their elementary divisors.

4·5.   We now proceed to show that these criteria are sufficient. We assume that (82) are satisfied (for every t) and then prove that the following particular transformation.

$$\eta_{lq_t} = \sum\limits_{r=1}^{n_t} \mathrm{T}_{qt}{}^{tts} \xi_{ts} \tag{83}$$

where the η's are taken as the initial vectors generating components, transforms $\lambda \mathrm{A}_t + \mu \mathrm{B}_t$, i.e., the direct sum of all the irreducible components having the elementary divisor ϕ^{r_t} into a form which is congruent with the corresponding $\lambda \mathrm{A}_t{}^* + \mu \mathrm{B}_t{}^*$; provided that $\mathrm{T}_{q_t t}{}^{tts}$ satisfy the equations (73) and the remaining coefficients in $\mathrm{T}_{q_t t}{}^{tts}$ are suitably chosen. We fix t and write the various quantities omitting the indices t as at the beginning of (4·4). We now show more precisely that:

the coefficients $T_{qv}{}^s$, $0 < v \leqslant r$, $n \geqslant s > q \geqslant 1$, *can be chosen so that*

$$\eta_u{}'B\phi^t J^k \eta_v = 0, \; 0 < k < m, \; 0 \leqslant l < r, \; 1 \leqslant v < u \leqslant n, \tag{84}$$

the other coefficients of the transformation (83) *being arbitrarily fixed in advance.*

Proof.—The determinant $|T_{qv}{}^s|$ considered as a polynomial in $J + 0$ (mod ϕ). For, if it were to vanish (mod $|\tau_q{}^s|$ defined in (79) would be singular But $|\tau_q{}^s|$ transforms one diagonal non-singular matrix to another of the same rank in K (θ) Hence $|\tau_q{}^s|$ is non-singular and consequently $|T_{qv}{}^s| + 0$ (mod ϕ). We now permute $\xi_1, \xi_2, \ldots \xi_n$ among themselves so that the first principal minor of $|T_{qv}{}^s|$, the first principal minor of this minor and so on are $+ 0$ (mod ϕ). We assume that $T_{qh}{}^s$ for $h = 1, 2, 3, \ldots g-1, n > s > q \geqslant 1$ have been chosen so that (84) is satisfied for $r > t > r-g-1$, and prove by induction on h, that $T_{qg}{}^r$, for $n \geqslant s > q \geqslant 1$ can be so chosen that

$$\eta_u{}'B\phi^{r-g-1} J^k \eta_v = 0, \; \text{for } 0 < k < m, \; \text{and } n > u > v \geqslant 1. \tag{85}$$

[As $\phi^r \xi_i = 0$ it easily follows that the L.H.S. of (85) depends only on $T_{qh}{}^r$ for $h \leqslant g$] Assume now that $T_{qu}{}^s$ for $n \geqslant s > q > w$ have been chosen so that

$$\eta_u{}'B\phi^{r-g-1} J^k \eta_v = 0, \; \text{for } n \geqslant u > v > w, \; 0 < k < m, \tag{86}$$

we show that it is possible to choose $T_{wg}{}^s$, $n \geqslant s > w$, so that

$$\eta_u{}'B\phi^{r-g-1} J^k \eta_w = 0, \; \text{for } n > u > w, \; 0 < k < m \tag{87}$$

[Induction on the decreasing values of w] In (87) we substitute for the η their expansions in terms of the ξ given in (83) and obtain, after the vanishing terms are omitted [$\phi^r \xi_i = 0$ for $i > r$] the following equation to determine $T_{wg}{}^s$:

$$\eta_u{}'B\phi^{r-g-1} J^k \eta_{wj} = \sum_{s=w+1}^{n} \xi_s{}'BJ^k T_{w0}{}^s T_{wg}{}^s \phi^{r-1}\xi_s + L = 0 \tag{88}$$

where L is a quantity which depends on the elements determined earlier. We show that $T_{wg}{}^s$, $n \geqslant s > w$, can be so chosen that (88) and (87) is true. Now $T_{wg}{}^s$ are polynomials of degree $< m$ in J and the equations (88) are a set of $(n - w) m$ linear equations in exactly the same number of unknowns. These have a solution $[T_{wg}{}^s = 0$ is also an admissible solution] except when polynomials ψ_s [at least one $\psi_s + 0$ (mod ϕ)] exist satisfying the equation

$$\sum_{s=w+1}^{n} \xi_s{}'BJ^k \psi_s \phi^{r-1} T_{u0}{}^s\xi_s = 0, \; w < u \leqslant n, \; 0 \leqslant k < m \tag{89}$$

and therefore

$$\sum_{u=w+1, \, s=w+1}^{n} \xi_s{}' B\psi_s \phi^{r-1} J^k f_u T_{u0}{}^s\xi = 0 \tag{90}$$

A6

for any arbitrary polynomials f_u in J. As $d = |T_{u0}{}^{s}|_{w<s,\,u\leqslant n} \neq 0$, on account of the particular permutation of the ξ_i's which was adopted, we choose f_u so that

$$\sum_{n=w+1}^{n} f_u \, T_{u0}{}^{s} = \delta_{sl} \cdot d \tag{91}$$

where l is chosen so that $\overset{l}{\psi_l} \neq 0 \pmod{\phi}$. Then (90) reduces to

$$\xi_l' B \phi^{r-1} J^k \, \psi_l \, \xi_l = 0, \; 0 < k < m \tag{92}$$

If $\psi_l = \sum_{k=0}^{m-1} t_k J^k$, we obtain from (92), that

$$\sum_{0}^{m-1} t_k \, i_{l,\,k+s} = 0, \text{ for } 0 \leqslant s < m \tag{93}$$

where $i_{hl} = \xi_l' B \phi^{r-1} \xi_l$.

It follows from (93) that $|I_{l0}| = 0$, *i.e.*, B is singular which is not true. Hence the $T_{qv}{}^{r}$ can be chosen so that $\lambda A_l + \mu B_l$ are transformed to the direct sum of n_l components corresponding to the same elementary divisor ϕ^{r_l}; each one of these n_l components are generated by

$$(i_{ql0}{}^{*}, i_{ql1}{}^{*}, \ldots i_{ql(m-1)}{}^{*}), \; 1 < q_l < n_l,$$

[*cf.* Definition $2 \cdot 2 \cdot 1$] which are congruent to the irreducible components of the $\lambda A^{*} + \mu B^{*}$. Thus the sufficiency of the criteria is proved.

REFERENCES

Dickson (I)	.	*Trans. Amer. Math. Soc*, 1909, **10**, 347–60
Albert (I)		*Ibid*, 1938, **43**, 386–436.
Williamson (I)		*Amer Jour of Math*, 1935, **57**, 475–90
———— (II)		*Ibid*, 1936, **58**, 141–63.
———— (III)		*Ibid.*, 1937, **59**, 399–413.

STUDIES ON THE DEPENDENCE OF OPTICAL
ROTATORY POWER ON CHEMICAL CONSTITUTION

Part XXVI. The Rotatory Dispersion of Salts of Camphor-
β-Sulphonic Acids with o-, m-, and p- Chloranilines

By Bawa Kartar Singh and Onkar Nath Perti

(Chemistry Department, University of Allahabad)

THE present communication is a continuation of Parts XXIII[1] and XXV[2] of this series and consists in the determination of optical rotatory dispersion of camphor-β-sulphonates of o-, m- and p-chloranilines. The object of this paper is to study the effect of substituting the electronegative group chlorine for hydrogen in o-, m- and p-positions in the benzene ring of the anilinocamphor-β-sulphonates and to compare its effect with that of methyl group when similarly substituted; incidentally also to study the effect of the position isomerides on optical rotatory power. The measurements of rotatory power were carried out for a number of wave-lengths in the visible region of the spectrum (4358 Å.U. to 6708 Å U) and in each case in four solvents. The influence of the nature of the solvent and wave-length of light on rotatory power has also been discussed.

Our previous studies[1,2] have shown that primary amine salts of d- or l-camphor-β-sulphonic acids undergo mutarotation in non-aqueous solvents owing to a structural change in the salt into ketimine or anil This view is further supported by our present studies since it is found that d- or l-forms of o-, m- and p-chloranilino-camphor-β-sulphonates, all primary amine salts, undergo mutarotation in non-aqueous solvents (vide Tables IV to VI).

INFLUENCE OF CHEMICAL CONSTITUTION ON ROTATORY DISPERSION

Rotatory dispersions have been classified as "simple" or "complex" according as they can or cannot be expressed by Drude's one-term equation, $[\alpha] = \frac{K}{\lambda^2 - \lambda_0^2}$. Though the optically active camphor-β-sulphonic acid exhibits complex dispersion,[3] many of its amine salts show simple dispersion.[1,2] The optically active o-, m- and p-chloranilino-camphor-β-sulphonates studied in the present paper were found to obey the simple dispersion formula exactly. On plotting $1/\alpha$ against λ^2 straight lines were

265

obtained in each case. We, however, also applied the more stringent numerical test by working out the dispersion equations and the results are recorded in Tables IV to VI. The differences between the observed specific rotatory power (o) and that calculated (c) from the dispersion equation are well within the limits of experimental error allowable in such measurements. For the sake of economy of space these differences (o-c) are not given in the tables.

In Drude's equation, $[\alpha] = \dfrac{K}{\lambda^2 - \lambda_0^2}$, K the rotation constant refers to that value of λ where $\lambda^2 - \lambda_0^2 = 1$ square micron, a value which is always found to lie in the infra-red region slightly greater than 10,000 Å.U. The constant K which is independent of the wave-length, is termed the absolute rotation of the compound. The longest observed wave-length in our measurements is 6,708 Å U. and an extrapolation from it to about 10,000 Å U. is easily permissible in view of the simple nature of the dispersion. In Table I, rotations are given for $[\alpha]_{5461}^{15^\circ}$ and the values of K, as a measure of the absolute rotatory power of the substance, are also given within brackets.

The Effect of $-CH_3$ and $-Cl$ Groups on Rotatory Power

Substituent groups may be arranged in accordance with the following polar series deduced from measurements of inductive capacities[4]:

$$O\overset{-}{H}, Cl, Br, I, C_6H_5, C\overset{-}{H_3}, \overset{+}{H}, COOH, CHO, COCH_3, CN, N\overset{+}{O_2}.$$
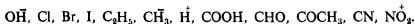
Since polar effect is traceable in optical activity[5] it is found that in general a positive group increases the rotation and a negative group causes a decrease in rotation, and further, the magnitude of the change, in general, corresponds to the series given above.

In Table I a comparison is made of the effects of electronegative $-CH_3$ and $-Cl$ groups. On comparing the values of $[\alpha]_{5461}$ in case of ortho substituent it is found that substitution of electronegative $-Cl$ for $-H$ causes a decrease in rotation in all the four solvents examined. Further, the decrease caused by the more electronegative $-Cl$ is greater than that caused by the less electronegative $-CH_3$. Similar results are obtained if a comparison is made for the values of K with the exception that in pyridine the order of K is $-Cl <-H <-CH_3$. In the case of meta substituent on comparing the values of $[\alpha]_{5461}$ the order of increasing rotation in ethyl alcohol and pyridine is $-Cl <-CH_3 <-H$, in water and methyl alcohol $-CH_3 <-Cl <-H$. The order of K in ethyl alcohol is $-CH_3 <-Cl <-H$, in pyridine $-Cl <-H <-CH_3$, and in water and methyl alcohol $-CH_3 <-H <-Cl$. In the case of para substituent the

order of $[\alpha]_{5\ 61}$ in water and ethyl alcohol is $-Cl < -CH_3 < -H$, in methyl alcohol $-CH_3 < -Cl < -H$ and in pyridine $-Cl < -H < -CH_3$. Comparison of the values of K shows that in water the order is $-CH_3 < -H < -Cl$, in methyl alcohol $CH_3 < -Cl < -H$, and in ethyl alcohol and pyridine $-Cl < -H < -CH_3$.

TABLE I

Structural formula ·	$[\alpha]_{5461}$ in solvent			
	Water	Methyl alcohol	Ethyl alcohol	Pyridine
1. †R SO₃H·H₃N⟨⟩* CH₃	20 50† (3 400)	32 40 (6 284)	36 40 (6 997)	36·10 (7·57)
2. R SO₃H·H₃N⟨⟩* Cl	19 87 (3 367)	29 60 (5 685)	34·74 (6 88)	36 20 (7·93)
3. R·SO₃H·H₃N⟨⟩* CH₃	18 97 (3 078)	26 96 (4 251)	28·97 (5 058)	32·50 (5·379)
4. R SO₃H H₃N⟨⟩* Cl	18 80 (3 31)	28 90 (5 661)	34 10 (6 79)	35·50 (7 74)
5 R SO₃H H₃N⟨⟩	20 00 (3 644)	32 00 (6 386)	34 00 (6 945)	34 46 (6 541)
6 R SO₃H·H₃N⟨⟩—CH₃*	20·20 (3 39)	30 47 (5 96)	35·50 (6 95)	37 60 (7 8')
7 R SO₃H H₃N⟨⟩—Cl	18 98 (3 510)	31 50 (6 276)	31 50 (6 689)	36 00 (6 42)

† The values of K are given within brackets.

$$CH_3—$$
$$H_3C—\ \ —C\ \ —CO$$
‡ R = $C_{16}H_{19}O$, or ⎰ $H_3C—C—CH_3$
$$H_3C\ \ —CH—CH.$$
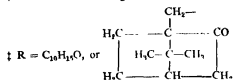
* B K. Singh, O N. Peru and B, N. Singh, *Proc. Lah ie Phil Soc.*, 1944, 6, 15, *Allahabad University Studies*, 1944, 37.

From the above it is evident that the greatest accord in rotatory power with the polar effect is found in the case of *ortho* substituent as might be expected from the close proximity of the groups involved to the asymmetric centre in the molecule.

THE EFFECT OF POSITION ISOMERISM ON ROTATORY POWER

In Table II the order of rotatory power of position isomerides in different solvents for $[\alpha]_{5461}^{25°}$ is given, the order of K is also given within square brackets.

TABLE II

Solvent	$[\alpha]_{5461}^{25°}$
Water	$\begin{cases} o- < p- < m- < Un- \\ [o- < p- < m- < Un-] \end{cases}$
Methyl Alcohol	$\begin{cases} o- < p- < m- < Un- \\ [o- < p- < Un- < m-] \end{cases}$
Ethyl Alcohol	$\begin{cases} o- < p- < m- < Un- \\ [o- < p- < m- < Un-] \end{cases}$
Pyridine	$\begin{cases} o- < m- < p- < Un- \\ [o- < p- < m- < Un-] \end{cases}$

On comparing values of $[\alpha]_{5461}^{25°}$ the sequence of position isomerides in all the solvents is $o- < p- < m- < Un-$ with the exception that in pyridine the order is $o- < m- < p- < Un-$. Similar results, with minor differences, follow when a comparison is made for the values of K (given in square brackets): the order of position isomerides in water, ethyl alcohol and pyridine is $o- < p- < m- < Un-$ and in methyl alcohol the sequence is $o- < p- < Un- < m-$. These results do not conform either to Frankland's[3] "lever arm" hypothesis or with its electrostatic modification as suggested by Rule[7] according to both of which meta isomer should be intermediate between the ortho and para.

THE PHYSICAL IDENTITY OF ENANTIOMERS

In our previous studies[1,2] in this series, Pasteur's Law of Molecular Dissymmetry according to which the d- and l- forms of a substance possess identical physical properties as regards their magnitude, has been found to hold good. Our present measurements of rotatory dispersion given in Tables IV to VI further support this law. Out of 280 observations recorded in this paper in as many as 248 cases the difference corresponds to a deviation of 0·02" or less in the observed angle of rotation which is the limit of experimental error allowable in such measurements. Only in 24 cases the difference corresponds to between 0·02° and 0 03°, and in 8 cases, all for Hg$_{4358}$ a difficult line to read, this difference lies between 0·03° and 0·05°. All these are, however, of the nature of casual experimental errors.

TABLE III

Line	[M]$^{550}_{\lambda}$ in aqueous solution for Camphor-β-sulphonates of :		
	o-ch'oranil'ine (1·0016 gm./100 c.c.)	m-chlorani'ine (1·0000 gm./100 c.c.)	p-chloraniline (1·000 gm./100 c.c.)
Hg₅₄₆₁	197·4	177·9	167·0
L₄₆₀₈	143·5	140·3	129·3
Cd₄₆₇₈	131·0	125·8	118·5
Cd₄₈₀₀	116·6	115·0	107·7
Cd₅₀₈₆	89·74	93·48	88·00
A₅₈₉₀	82·54	82·68	79·02
Hg₅₄₆₁	68·21	71·90	68·25
Hg₅₇₉₀	55·62	61·10	57·49
Na₅₈₉₃	51·98	55·72	53·91
L₆₁₀₄	44·86	50·32	48·50
Cd₆₄₃₄	41·27	44·93	43·11
Li₆₇₀₈	32·28	35·95	36·95

TABLE IV.   o-*Chloranilino-camphor-β-sulphonates*

Solvent	Water	Methyl alcohol	Ethyl alcohol	Pyridine
Concentration in gm./100 c c { d- / l- }	1·0016 / 1·0000	1·0016 / 1·0000	1·0008 / 1·0016	1·0000 / 1·0016
Calculated { $[\alpha]$ / λ_0 }	± $\dfrac{3\,078}{\lambda^2 - 0·1356}$ 0·3682	± $\dfrac{4·251}{\lambda^2 - 0\,1408}$ 0·3752	± $\dfrac{5\,058}{\lambda^2 - 0·1203}$ 0·3468	± $\dfrac{5\,379}{\lambda^2 - 0·1327}$ 0·3642

Line	Obs $[\alpha]^{18°}$		Obs $[\alpha]^{18°}$		Obs $[\alpha]^{18°}$		Obs $[\alpha]^{18°}$	
	d-	l-	d-	l-	d-	l-	d-	l-
Hg₅₄₆₁	+54 91°	−57 00°	+87·86°	−87 00°	+73 44°	−71 88°	+67 50°	−68 80°
L₄₆₀₈	39 93	41·00	58 90	60 00	54 96	55 91	62 00	62 89
Cd₄₆₇₈	36 44	37 00	54 91	54 00	49 46	50 92	55 50	54 91
Cd₄₈₀₀	32 44	32 00	46·92	47 00	45 46	46 42	52 50	52 43
Cd₅₀₈₆	24 96	24 50	36 44	36 50	35 97	35 94	42·50	42·43
A₅₈₉₀	22 96	22 00	32 44	32 00	33 97	32 04	39 50	38 44
Hg₅₄₆₁	18 97	18 50	26 96	27 50	28 97	28 95	32 50	32 44
Hg₅₇₉₀	15 47	15·50	22 41	22 50	23·98	23 96	27 00	26 95
Na₅₈₉₃	14·47	14·50	20·46	20 00	22 48	22·48	24 50	24 96
L₆₁₀₄	12 48	13 00	18·47	18·00	19 48	19 98	23 00	23 48
Cd₆₄₃₄	11·48	11 00	14 97	16 00	16·98	17 47	19·00	18 47
Li₆₇₀₈	8·98	9·00	12 98	13·50	15·49	14·99	17·50	16 97
	No mutarotation		Shows mutarotation. Rotation for d-salt after 23½ hrs. $[\alpha]^{550}_{5461}$ = + 23·46° and for l-salt after 23 hrs $[\alpha]^{350}_{5461}$ = − 24·00°		Shows mutarotation. Rotation for d-salt after 23 hrs $[\alpha]^{350}_{5461}$ = + 25·98° and for l-salt after 21 hrs $[\alpha]^{350}_{5461}$ = − 26·46°		Shows mutarotation. Rotation for d-salt after 46½ hrs $[\alpha]^{550}_{5461}$ = + 29·00° and for l-salt after 47½ hrs. $[\alpha]^{550}_{5461}$ = − 28 45°	

TABLE V. m-*Chloranilino-camphor-β-sulphonates*

Solvent	Water	Methyl alcohol	Ethyl alcohol	Pyridine
Concentration {d-} {l-} in gm/100 c c	1·0030 1·0008	1 0000 1·0016	1·0000 1 0008	1·0008 1·0016
Calculated {[a]} {λ_0}	± $\dfrac{3\ 644}{\lambda^2 - 0\ 116j}$ 0·3406	± $\dfrac{6·386}{\lambda^2 - 0\ 0987}$ 0·3142	± $\dfrac{6·945}{\lambda^2 - 0\ 0937}$ 0·3061	± $\dfrac{6·541}{\lambda^2 - 0\ 1055}$ 0·3248

Line	Obs [a]⁸⁶° d-	l-	Obs [a]⁸⁶° d-	l-	Obs. [a]⁸⁶° d-	l-	Obs [a]⁸⁶° d-	l-
Hg_{5458}	+49 50°	18 96°	+71 00°	−69 38°	+72 00°	−72 94°	+60 95°	−61 90°
L_{5878}	39 00	38 47	55 50	55 91	59·50	58 95	57 96	57 40
C_{5876}	15 00	35 97	53 00	52 91	51 00	54 96	52 97	51·92
Cd_{5461}	32 07	31 47	48·00	48 92	42 00	41 96	43 96	43·43
Cd_{5086}	26 00	25 48	39 50	40 44	39 50	38 96	39 97	39·43
A_{5890}	23 00	22 98	37·00	36 44	34 00	33·97	34·46	33·94
Hg_{5461}	20 00	19 48	32 00	32·44	29 50	28 97	28 48	28 95
H_{5790}	17 00	16·99	28 00	27 95	27 00	26 97	26·98	26 96
N_{5892}	15 50	15 99	26 00	25·46	25 00	24 48	24·48	24 96
L_{5104}	14 00	14 49	23·00	23 48	21 00	21·98	20 98	20 98
Cd_{4638}	12 50	11 99	20 50	19 96	19 00	18 98	17 98	18 47
L_{4708}	10 00	10 00	18 00	17·47				

Water: No mutarotation

Methyl alcohol: Shows mutarotation. Rotation after 21½ hrs for d-salt [a]³⁵⁰_5461 = 28 00° and for l-salt [a]³⁵⁰_5461 = −28·45°

Ethyl alcohol: Shows mutarotation. Rotation for d-salt after 22 hrs [a]³⁵⁰_5461 = + 31·00° and for l-salt after 26½ hrs [a]³⁵⁰_5461 = − 30·47°

Pyridine: Shows mutarotation. Rotation after 22 hrs. for d-salt [a]³⁵⁰_5461 = 31·97° and for l-salt [a]³⁵⁰_5461 = − 31·94°.

THE NATURE OF RACEMIC MODIFICATION

The melting points of racemic forms of o-, m- and p-chloranilino-camphor-β-sulphonates are higher than those of the optically active forms. These racemic forms are, therefore, true dl-compounds in the solid state.

THE EFFECT OF SOLVENT ON ROTATORY POWER

It is observed that the order of decreasing rotatory power of the position isomerides of chloranilino-camphor-β-sulphonates for Hg₅ ₆₁ (Table I, Nos. 3, 5, 7) in solvents is pyridine > ethyl alcohol > methyl alcohol > water, whereas the sequence of increasing dielectric constant of the solvents is pyridine (12·4) < ethyl alcohol (25·8) < methyl alcohol (31·2) < water (80). Hence it is obvious that the sequence of dielectric constant of the solvents follows the same order as that of rotatory power but in the opposite sense. It would, however, be more rational to compare the rotatory power of a substance with the dielectric constant of its solution

TABLE VI. p-*Chloranilino-camphor-β-sulphonates*

Solvent	Water		Methyl alcohol		Ethyl alcohol		Pyridine	
Concentration $\begin{cases}d-\\l-\end{cases}$ in gm./100 c.c.	1·0008	1·0000	1·0000	1·0008	1·0000	1·0000	1·0000	1·0016
Calculated $\begin{cases}[\alpha]\\\\\lambda_0\end{cases}$	$\pm \dfrac{3\cdot510}{\lambda^2-0\cdot1135}$ 0·3369		$\pm \dfrac{6\cdot276}{\lambda^2-0\cdot1016}$ 0·3187		$\pm \dfrac{6\cdot689}{\lambda^2-0\cdot0985}$ 0·3138		$\pm \dfrac{6\cdot42}{\lambda^2-0\cdot1200}$ 0·3464	
Line	Obs. $[\alpha]^{35°}$		Obs. $[\alpha]^{35°}$		Obs. $[\alpha]^{35°}$		Obs. $[\alpha]^{35°}$	
	d-	l-	d-	l-	d-	l-	d-	l-
Hg_{5460}	+46 46°	−45 00°	+71·50°	−69 94°	+74 00°	−72 50°		
L_{4608}	35 97	36 50	56 50	57 45	58·50	59 50		
Cd_{6438}	32 97	33 50	54·00	52 96	55 50	56 00	+64 50°	−65·39°
Cd_{6099}	29 97	30 50	48 50	48 96	51 00	50 50	58 50	57·91
Cd_{5086}	24·48	24 00	40 00	40 46	42 50	42 00	46·50	46·92
A_{5606}	21·98	22 00	37 00	36 47	43·50	39 50	42 50	41 93
Hg_{5461}	18 98	19·00	31·50	31·97	33 50	33 50	36 00	36·44
$H_{5079·9}$	15 99	16·00	27·50	26·97	29 00	28 50	30·00	30 45
N_{4931}	14 99	15 00	25·00	24 98	26·00	25 50	28 00	28 45
L_{4194}	13·49	14·00	23 00	23 48	24 50	24 00	25 00	24·96
Cd_{4164}	11 99	11·50	20 50	19 98	21 00	21·50	22 50	21·46
L_{4101}	10 00	10·50	17 50	17·48	18 50	18 50	19 00	18 96
	No mutarotation		Shows mutarotation. Rotation for d-salt after 23 hrs $[\alpha]^{350}_{5461}$ = +28 50° and for l-salt after 24 hrs $[\alpha]^{350}_{5461}$ = −−28·47°.		Shows mutarotation. Rotation for d-salt after 24 hrs $[\alpha]^{350}_{5461}$ =31·50° and for l-salt after 23 hrs $[\alpha]^{350}_{5461}$ −− 32 00°.		Shows mutarotation. Rotation for d-salt after 24 hrs $[\alpha]^{350}_{5461}$ = +33·50° and for l-salt after 23¼ hrs $[\alpha]^{350}_{5461}$ −− 33 44°.	

and not of the solvent in which the rotatory power is determined. We have used the values of the dielectric constants of the solvents because we have not at our disposal the values of the dielectric constants of the solution.

THE MOLECULAR ROTATORY DISPERSIONS OF CAMPHOR-β-SULPHONATES IN AQUEOUS SOLUTION AND COMPARISON OF THE VALUE OF $[M]_D$ OF CAMPHOR-β-SULPHONATE ION IN WATER

In Table III are given the values of $[M]_D^{35°}$ in water for camphor-β-sulphonates of o-, m- and p-chloranilines. The mean value for camphor-β-sulphonate ion in water is $[M]_D = 52°.8$ The values of $[M]_D^{25°}$ for o-, m- and p-chloranilino-camphor-β-sulphonates are 51·98, 55·72 and 53·91 respectively. This shows that o- and p-chloranilino salts are fairly completely dissociated in 1% solution and the m-chloranilino salt is less dissociated. A strict comparison would require, however, a knowledge of degree of

ionisation of salts with dilution since the observed molecular rotation is due both to the active ion and to the non-ionised molecule.

Experimental

Chloranilino-camphor-β-sulphonates.—Molar amounts of each of the base and the camphor-β-sulphonic acids were dissolved separately in hot ethyl acetate. The two solutions were then mixed and allowed to stand when the salts crystallised out. They were then repeatedly crystallised from a mixture of ethyl alcohol and ethyl acetate. They were dried at 80° in an air oven and then in vacuum. All the salts are white crystalline products.

o-Chloranilino-camphor-β-sulphonates.—They are readily soluble in ethyl alcohol, methyl alcohol, acetone, chloroform, pyridine and water; less so in ethyl acetate, and insoluble in benzene, ether and petroleum ether. (Found: *d*-salt, m p. 132–133° C, eq. wt. = 358·8, S = 8·99%; *l*-salt, m.p. 132–33° C., eq wt. = 360·6, S = 8·78%; *dl*-salt, m p. 142–143° C, eq. wt. = 356·6, S = 8·85%; $C_{10}H_{15}OSO_3H \cdot H_2NC_6H_4Cl$ requires eq. wt. = 359·5, S = 8·90%.)

m-Chloranilino-camphor-β-sulphonates.—All the salts are freely soluble in ethyl alcohol, methyl alcohol, water and pyridine; less so in ethyl acetate, and insoluble in benzene, ether and petroleum ether. (Found: *d*-salt, m p. 159–160° C, eq. wt. = 358·7, S = 9 00%, N = 3·87%; *l*-salt, m.p. 159–160° C, eq. wt = 362 1, S = 8 91%, N = 4·09%; *dl*-salt, m.p. 164–165° C, eq. wt = 359·3, S = 8·73%, N = 3·57%; $C_{10}H_{15}OSO_3H \cdot H_2N C_6H_4Cl$ requires eq. wt. = 359·5; S = 8 90%; N = 3·89%)

p-Chloranilino-camphor-β-sulphonates.—All the three salts are readily soluble in pyridine, methyl alcohol, chloroform, ethyl alcohol and water; less so in ethyl acetate, acetone and benzene, and insoluble in ether and petroleum ether. (Found: *d*-salt, m.p. 158° C., eq wt. = 355·6, S = 9·10%; *l*-salt, m.p. 158° C., eq. wt = 362 9, S = 9·12%; *dl*-salt, m.p. 161–162° C, eq. wt. = 357·0, S = 8·70%; $C_{10}H_{15}OSO_3H \cdot H_2NC_6H_4Cl$ requires eq. wt. = 359·5; S = 8·90%)

The rotatory power determinations were carried out in a 2-dcm. jacketed tube at 35° C. The values of λ_0, calculated from the dispersion formulæ, are given in Tables IV to VI and are expressed as μ or 10^{-4} cm.

References

1. B. K. Singh, O. N. Perti and   *Proc. Lahore Phil. Soc.*, 1944, **6**, 15,
   B. N. Singh   *Allahabad University Studies*, 1944, 37.
2. B. K. Singh and O. N. Perti   *Proc. Ind. Acad. Sci.*, (A) 1945, **22**, 84.
3. Richards and Lowry   *Jour Chem Soc.*, 1925, **127**, 1511.
4. Rule   *Ibid*, 1924, **125**, 1121.
5. B K Singh and B. N Bhaduri   *Proc Ind Acad Sci*, (A), 1937, **6**, 340;
                                    1939, **10**, 359, etc.
   Betti   *Gazz. Chem. Ital*, 1923, **53**, 424.
6 Frankland   *Jour Chem Soc.*, 1896, **69**, 1583
   B K. Singh and Majumdar   *Ibid*, 1919, **115**, 567
7. Rule   . *Ibid*, 1924, **125**, 1122.
8 Thomas and Jones   ..   *Ibid*, 1906, **89**, 284.

RAMAN SPECTRA OF THE SECOND ORDER
IN CRYSTALS

Part II. Gypsum

BY R. S. KRISHNAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

1. PREVIOUS WORK ON GYPSUM

THE Raman spectrum of gypsum has been studied in some detail by numerous investigators As usual, most of the earlier work was confined to the cataloguing the frequency shifts of the Raman lines in gypsum and estimating their relative intensities, viz., Krishnan (1929), Hollænder and Williams (1929, 1931), Dickinson and Dillon (1929), Nisi (1929), Schæfer, Matossi and Aderhold (1929, 1930a), Krishnamurti (1930) and Rasetti (1931, 1932).

The effect of crystal orientation on the intensity and/or polarisation of the Raman lines of single crystals of gypsum was investigated by Schæfer, Matossi and Aderhold (1930b, c), Nisi (1931), Cabannes (1932, 1938), Aynard (1940), Roop Kishore (1942) and Cabannes and Aynard (1942) using incident unpolarised light, and by Saksena (1941), Rao (1941) and Rousset and Lochet (1945) using incident polarised light. Among them Nisi (1931) and Roop Kishore (1942) confined themselves to the study of the variations of the intensities of the Raman lines for different orientations of the crystal. Schæfer, Matossi and Aderhold, Saksena and Rao investigated in particular the intensities and depolarisations of the Raman lines corresponding to the internal oscillations of the SO_4 ions and to the oscillations of the water molecules

Cabannes (1932) and Rousset and Lochet (1945) made a special study of the frequencies characteristic of the SO_4 ions in gypsum. Rousset and Lochet recorded nine Raman lines due to the SO_4 ion, the frequency shifts being 413, 492, 621, 623 5, 669, 1006, 1117, 1138 and 1144 wave numbers. Thus the results of Rousset and Lochet are the most complete as regards the fundamental frequencies of the SO_4 ions are concerned. From an analysis of the polarisation data, they have concluded that the lines 413, 492, 621, 1006 and 1144 cm.$^{-1}$ come under the symmetric class, while the rest come under the antisymmetric class.

274

Cabannes (1938) and Aynard (1940) made a detailed study of the Raman water bands in gypsum. Aynard gave the frequency shifts of the water bands due to the stretching vibrations of the water molecules as 3404 (symmetric) and 3493 cm.$^{-1}$ (antisymmetric) and that of the deformation vibration as 1660 cm.$^{-1}$ Later, these two authors (1942) jointly worked out the Raman activity and depolarisation of the various co-operative vibrations of the water molecules in the unit cell of gypsum and compared the results obtained thereby with the experimental data

The results obtained by the numerous investigators quoted above show wide discrepancies especially with regard to the number and frequency shifts of the low frequency or lattice lines Rasetti (1932) using the 2536·5 mercury resonance radiation as exciter recorded as many as nine lattice lines, while those who employed the 4046 and 4358 radiations recorded only a couple of lines instead. Roop Kishore (1942) using the Rasetti technique and giving long exposures reported for the first time the existence of a weak line at 1622 cm^{-1}, a weak band at about 2249 cm^{-1} and three more weak water bands with mean frequency shifts 3244, 3309 and 3584 cm^{-1} in the neighbourhood of the two principal water bands.

In continuation of the work on calcite (Krishnan, 1945), the author has now undertaken a detailed study of the Raman effect in gypsum using the mercury resonance radiation λ 2536 5 as exciter in order to record the first order spectrum in all its detail, and also to get some data regarding the second order spectrum in gypsum The results are presented in this paper.

2 DETAILS OF THE EXPERIMENT

The technique of using the mercury resonance radiation λ 2536·5 for exciting the Raman spectrum of a crystal has already been described in some of the earlier papers of the author. A transparent crystal of gypsum in the form of a triangular disc (4½" side and ⅜" thick) was selected for the present investigation from Sir C. V. Raman's personal collection The flat faces were parallel to the cleavage plane In all the experiments the specimen was illuminated with unpolarised light through one of its flat faces and the scattered light was photographed through one of its edges.

As in the case of calcite, two different instruments were used for recording the Raman spectra: (1) A Hilger E1 quartz spectrograph and (2) a Hilger E3 quartz spectrograph. The high dispersion instrument was used in order to record the lattice and SO_4 spectra in all their detail and also to measure the frequency shifts and widths of the lattice and SO_4 lines very accurately. For this purpose an iron arc comparison spectrum was taken on the same

negative partially overlapping the Raman spectrum. Using a slit width of 0·04 mm. exposures of the order of three days were given in order to get a spectrogram showing the lines with reasonable intensity.

The E3 quartz spectrograph was used to get intense photographs of the complete Raman spectrum of gypsum. With a slit width of 0·03 mm. exposures of the order of two days were given to record intense spectrograms, a sample of which is reproduced in Fig. 1 (a).

3. RESULTS

The spectrograms and the microphotometric records of some of them are reproduced in Figs. 1 to 5. Descriptions of the figures are given at the end of this paper. The positions and the frequency shifts of the Raman lines are marked in the figures. Most of the Raman lines have also been recorded on the anti-Stokes side.

In Table I are listed the frequency shifts of the Raman lines observed in the various spectrograms obtained in the present investigation. The shifts of the first 23 Raman lines and the widths of the most prominent of them have been measured from the spectrogram taken with the higher dispersion instrument and should therefore be considered as accurate. The temperature of the crystal was in the neighbourhood of 35°. The frequency shifts of the remaining Raman lines except the feeble ones at 1500, 2143 and 2268 cm.$^{-1}$ were evaluated from measurements made on the spectrogram taken with the E3 spectrograph. The frequency shifts of the three feebler lines have been estimated from the microphotometric record of this region of the spectrum. The values of the frequency shifts of the Raman lines of gypsum recorded earlier by Rasetti (1932), Saksena (1941), Roop Kishore (1942) and by Rousset and Lochet (1945) are included in Table I for purposes of comparison. The Raman spectrum recorded by the present author is more complete in respect of the lattice lines, the lines due to the sulphate ions and the water bands than any obtained by the earlier investigators. The lines with frequency shifts 565, 990, 1500, 2143, 2268 and 3680 cm.$^{-1}$ have been recorded for the first time.

The 34 Raman frequencies tabulated above have been classified into three groups namely, lattice spectrum denoted by l, the spectrum of the SO_4 ions in the crystal denoted by s and the spectrum of the water molecules denoted by w. The assignment of the lines into the group w was based particularly on considerations of their widths.

In addition to the Raman lines the positions of which have been marked in the figures there are indications of the existence of other feebler lines and

TABLE I

No.	Author Frequency shift in cm^{-1}	Width in cm^{-1}	Group	Rasetti (1932)	Saksena (1941)	Roop Kishore (1942)	Rousset and Lochet (1945)
1	32 (2)	..	*l*	37	..	.	..
2	59 (2)	..	*l*	60	..	56	..
3	93 (1)	..	*l*	..	80	.	..
4	110 (4)	3	*l*	110	..	101	..
5	121 (5)	3	*l*	122	125	.	..
6	132 (4)	2	*l*	134	.	..	..
7	145 (4)	2	*l*	146	.	145	..
8	162 (3)	2	*l*	164	..	.	..
9	180 (5)	3	*l*	182	175	180	..
10	211 (5)	4	*l*	211	.	210	..
11	315 (2)	12	*w*	.	.	315	..
12	415 (9)	3	*s*	415	415	416	413
13	492 (10)	4	*s*	495	492	492	492
14	565 (2)	20	*w*	..	.	.	..
15	588 (2)	20	*w*	.	585	588	..
16	618 (5)	3	*s*	.	.	620	621
17	622 (6)	3	*s*	.	.	.	623·5
18	672 (5)	3	*s*	..	672	672	669
19	990 (3)	3	*s*	.	.	.	..
20	1006 (30)	5	*s*	1009	1006	1004	1006
21	1115 (4)	4	*s*	.	1115	1115	1117
22	1136 (20)	4	*s*	1137	1136	1135	1138
23	1143 (4)	4	*s*	.	.	.	1144
24	1500 (1)	..	*c*	..	.	.	..
25	1631 (2)	..	*c*	..	..	1622	.
26	2143 (1)	..	*s*	..	.	..	.
27	2215 (2)	40	*w*	..	.	2249	.
28	2268 (1)	..	*s*	..	.	.	.
29	3258 (3)	15	*w*	..	..	3244	.
30	3334 (3)	15	*w*	.	.	3309	.
31	3406 (30)	15	*w*	3399	3406	3410	.
32	3495 (30)	15	*w*	3476*	3493	3480	..
33	3606 (3)	15	*w*	.	.	3584	..
34	3680 (2)	..	*w*	..	.	..	..

l—Means lattice oscillation   *s*—Oscillation of the SO$_4$ group.   *w*—Oscillation of the water molecules

The figures given within brackets represent visual estimates of the relative intensities of the lines.

* This is obtained from measurements made on the photographs reproduced in Rasetti's paper. The value given by Rasetti (1932) for this band is 3426 which should evidently be wrong.

In addition to those listed in the above table, there are a few more fainter lines and bands (*cf.* text).

bands. One such line falls in between the Raman lines at 162 and 180 cm.$^{-1}$ The existence of a broad band superposed on the four lattice lines at 110, 121, 132 and 145 cm.$^{-1}$ is discernible from an examination of Figs. 4 and 5. The lattice line with a frequency shift of 211 cm.$^{-1}$ has a feeble companion on the longer wavelength side (see Fig. 5).

The spectrograms of the mercury arc and of the Raman effect in gypsum which are reproduced in Figs. 2a and 2b, were taken under identical conditions. In the mercury arc photograph the λ 2536 5 line is much less intense than its companion, λ 2534 8, whereas in the scattered picture they are of comparable intensity although the same column of mercury vapour was used in both cases. The enhanced intensity of the unmodified line should be attributed to the presence of Brillouin components which are not absorbed by the column of mercury vapour. Similar observations have already been reported by the author in the case of calcite.

4 DISCUSSION

Gypsum is an ionic crystal and the unit cell which belongs to the monoclinic class contains four molecules of $CaSO_4.2H_2O$. There is a perfect cleavage plane parallel to the (010) face. The crystal possesses only one symmetry axis called the b-axis, which is perpendicular to the cleavage plane. The space group is C_{2h}^6. Wooster (1936) made a detailed X-ray analysis of the crystal structure of gypsum. The relevant details are quoted from his paper. " It is a layer lattice, layers being parallel to the face (010). Two sheets of SO_4 groups are intimately bound together by Ca ions so as to form a strong double sheet; successive double sheets are separated by sheets of water molecules. Each Ca atom is surrounded by six oxygen atoms belonging to the SO_4 groups and by two water molecules. Each water molecule links a Ca atom both to an oxygen in the same double sheet and to one in a neighbouring sheet. The latter bonds are comparatively weak and explain the easy cleavage parallel to the (010) face. The concentration of the water of crystallisation in sheets parallel to (010) is a very interesting feature ". Wooster's analysis shows that the four oxygen atoms belonging to the same sulphate group are situated at the corners of a regular tetrahedron. On the basis of the above structure let us proceed to discuss the results obtained from Raman effect studies.

Spectrum of the SO_4 ion —It is well known that the SO_4 ion in the free state, viz., in solutions of sulphates, has only four distinct modes of oscillation of which one is single, one doubly degenerate and the remaining two triply degenerate. The corresponding Raman frequencies are 983, 454, 622 and 1106 cm^{-1}. In gypsum the degeneracies of the frequencies belonging to the tetrahedral SO_4 ion are split up and the spectrum shows nine Raman lines, the frequency shifts of which are given below.

Raman Frequencies of SO_4 Ion

In the free state	..	454		622		983		1106	
In gypsum	..	415 492 ?		618 622 672 ,		1006 ,		1115, 1136 1144	

There are two possible explanations for the appearance of nine distinct modes as fundamentals in the Raman spectrum of the SO_4 ion in gypsum. The structure of the ion may be permanently distorted in the crystalline state so that it does not possess the full symmetry of the point group Td. In order to account for the depolarisation of the Raman lines observed by Rousset and Lochet (1945), the distorted ion should have only the symmetry of the point group C_2. This explanation was originally suggested by Cabannes (1932). On the basis of this picture when gypsum is dissolved in water, there should be an abrupt and violent change in the structure of SO_4 ion. *Prima facie* this view appears to be unreasonable. Moreover, the X-ray evidence is also inconsistent with the above point of view

The alternative is to assume that the SO_4 ion retains its tetrahedral structure in the crystalline state also During the internal oscillations of the ion, in addition to the valency forces between the constituent atoms in the ion, subsidiary forces due to the potential field of the neighbouring ions have to be taken into account in the crystal It is these forces operating against the freedom of movement of the constituent atoms of the ion that cause the splitting of the degenerate frequencies and also the enhancement of the non-degenerate ones The above explanation has been favoured by Bhagavantam (1938) and it appears to be a reasonable one He pointed out from a simple group theoretical analysis that the four distinct modes of oscillation appropriate to the free SO_4 ion split up into nine components on account of the lower symmetry of the crystal, the selection rules for the various components being entirely different among themselves and from those of the ion. This offers a satisfactory explanation for the observed polarisation characters of the SO_4 lines in gypsum, although the ion has the full tetrahedral symmetry when the atoms are at rest. Analogous quantitative explanation has already been offered with success in order to account for some of the features observed in the Raman spectra of crystalline nitrates.

The feeble lines with frequency shifts 990, 1500, 1631, 2143 and 2268 cm $^{-1}$ evidently belong to the second order Raman spectrum of the SO_4 ion in gypsum. These are assigned as octaves and combinations of the some of the nine fundamental frequencies of the SO_4 ion as indicated below:—

990	Octave	492 + 492
1500	Combination	1006 + 492
1631	Combination	1006 + 622
2143	Combination	1006 + 1136
2268	Octave	1136 + 1136

The lattice spectrum.—The mutual oscillations of the ions in the unit cell in which the SO_4 group and $2H_2O$ group act as entities constitute the

A7

lattice spectrum of gypsum. Neglecting the influence of the H_4O molecules on the mutual oscillations of the Ca and SO_4 ions, Bhagavantam (1938) has shown that there should be eighteen Raman active lattice oscillations in gypsum. On the other hand, the recorded spectrum consists of seven sharp, intense and closely spaced lattice lines and three relatively feebler lines with low frequency shifts. Further experimental work on the effect of crystal orientation on the intensity and polarisation of the lattice lines is called for in order to give satisfactory assignments to the observed lattice lines.

   The spectrum of water of crystallisation —On comparing the Raman bands of water in gypsum as observed in the present investigation with those of ordinary water and of ice (summarised in Hibben's book), we find that the number and distribution of the bands are common to all the three.

<div align="center">TABLE II</div>

<div align="center">*Frequency Shifts of Raman Bands*</div>

Gypsum	Ordinary water	Ice at 0° C
318	170	205
565 ⎱ 588 ⎰	500	600
1631	1650	1650
2215	2170	2225
3258 ⎱ 3334 ⎰ (m)	3231 (st)	3193
3406 ⎱ 3495 ⎰ (v. st)	3436 (v. st)	3391
3608 ⎱ 3680 ⎰ (m)	3605	3549

The correspondence follows as a natural consequence of the fact that in gypsum the water molecules are concentrated in separate sheets which are only loosely bound with other sheets of ions and as such the oscillations of the water molecules are not appreciably modified in the crystalline state. The bands in gypsum are very much sharper than those observed with ordinary water and consequently their maxima could be measured with a high degree of accuracy. The spectrum of gypsum shows another interesting feature. The three principal water bands are split into six fairly narrow bands. They form three pairs as shown in Table II. The difference in the frequency shifts of the two components of each pair is approximately constant for the three pairs, the average value being 80 wave numbers. The splitting of the principal water bands can be attributed to the low symmetry of gypsum crystal compared to that of ice. Results obtained by Cabannes (1938), Saksena (1941)

and Rao (1941) from polarisation studies indicate that the band at 3406 belongs to the symmetric class, while the one at 3495 belongs to antisymmetric class. Similar behaviour should be exhibited by the other two pairs of bands also. Because of the antisymmetric nature of the band at 3495 cm.$^{-1}$ Cabannes (1938) had suggested that this band should correspond to the Raman inactive valence vibration of the H_2O molecule, which was rendered active in the crystalline environment.

The Raman bands of water in several crystalline hydrates have been the subject of study by numerous investigators notably by Nisi (1931), Ananthakrishnan (1937), Hibben (1937), Canals and Peyrot (1938), Nayar (1938) and Lakshman Rao (1941). The results reported up to the end of 1938 have been summarised in Hibben's book (1939) The spectrum of water of crystallisation in gypsum as recorded by Roop Kishore and the present author shows far greater detail than any recorded by others not only in gypsum but in other crystalline hydrates as well. The success is due to the use of the intense mercury resonance radiation for exciting the Raman spectrum. A similar study with other crystalline hydrates would furnish us with valuable data which could be correlated with the physical properties of the molecules involved.

5. INFRA-RED SPECTRUM

Investigations on the infra-red spectrum of gypsum are very scanty. Kock (1908) who studied the nature of residual rays of gypsum reported the existence of a narrow intense band at 8 69 μ due to the SO_4 ion and a fairly broad one at about 24 μ. Coblentz (1910, 1911) made a detailed analysis of the high frequency infra-red absorption bands of the water of crystallisation in gypsum On the whole seven absorption maxima were observed by him. They are at 1·5 μ, 2·05 μ, 2·95 μ, 4·34 μ, 5·95 μ, 6·5 μ and 6·68 μ. The corresponding frequencies in wave numbers are 6666, 4880, 3390, 2200, 1680, 1540 and 1495.   Bands corresponding to 3390 and 2200 appear in the Raman spectrum of gypsum. Schaefer and Schubert (1916) investigated the infra-red absorption spectrum of gypsum in the region of the specific frequencies of the sulphate ion. They observed two strong absorption maxima at 8·74 μ (1144 cm.$^{-1}$) and at 14 84 μ (674 cm $^{-1}$) and a secondary maxima at 8·62 μ (1160 cm.$^{-1}$). The Raman lines corresponding to 8·74 μ and 14 84 μ infra-red bands have been observed with frequency shifts 1136 and 672 cm.$^{-1}$ As is to be expected, the depolarisation data given by Rousset and Lochet indicate that these two Raman lines come under the antisymmetric class.

In conclusion, the author wishes to express his grateful thanks to Professor Sir C. V. Raman for the loan of the crystal of gypsum and for his kind interest in the work.

6. SUMMARY

The earlier work on the Raman effect in gypsum has been briefly reviewed.

The results obtained from a detailed study of the Raman effect in gypsum using the mercury resonance radiation as exciter are described. The recorded spectrum consists of 34 Raman lines and bands distributed as follows: 10 lines belong to the lattice spectrum, 14 Raman lines constitute the spectrum of the SO_4 ion and ten Raman bands make up the spectrum due to the water of crystallisation. The frequency shifts and widths of most of them have been accurately determined. In addition to these, a few other fainter lines and bands have been recorded.

Of the 14 Raman lines belonging to the internal oscillations of the SO_4 ion, nine are comparatively more intense and they constitute the first order spectrum. On the basis of the known crystal structure of gypsum, the appearance of the nine lines as fundamentals has been satisfactorily explained. The five feebler lines have been assigned as octaves and combinations of the fundamental frequencies. They constitute the second order spectrum of the SO_4 ion. The Raman bands of water of crystallisation in gypsum exhibit some of the important features characteristic of the Raman bands of ordinary water and of ice. The similarity in the behaviour of the water bands has been attributed to the fact that the water molecules in gypsum are concentrated in separate sheets parallel to the cleavage face and are only loosely linked up with other ions.

The frequencies corresponding to the various maxima observed in the infra-red absorption spectrum of gypsum have been compared with those observed by the author in the Raman spectrum.

A complete bibliography on the Raman effect and infra-red studies in gypsum is also included.

REFERENCES

1. *Raman Effect*

Krishnan, K. S	*Ind Journ Phys.*, 1929, **4**, 131.	
Hollaender and Williams	*Phys. Rev.*, 1929, **34**, 994 , 1931, **38**, 1739.	
Dickinson and Dillon	..	*Proc. Nat. Acad. Sci., U.S.A.*, 1929, **15**, 695.
Nisi	*Proc. Imp. Acad. Tokyo*, 1929, **5**, 407.	
Schæfer, Matossi and Aderhold	*Phys. Zetts.*, 1929, **30**, 581 ; *Zetts. f. Phys.*, 1930a, **65**, 289.	

Fig. 1

Fig. 2
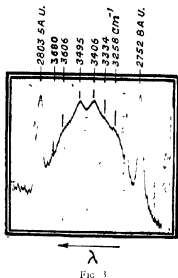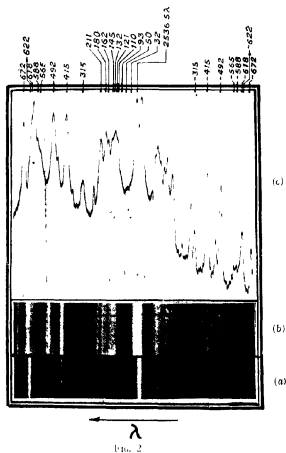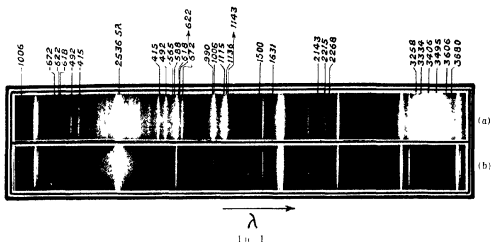
Fig. 3
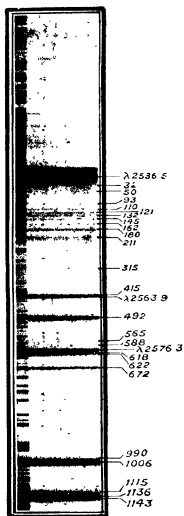
Fig. 4
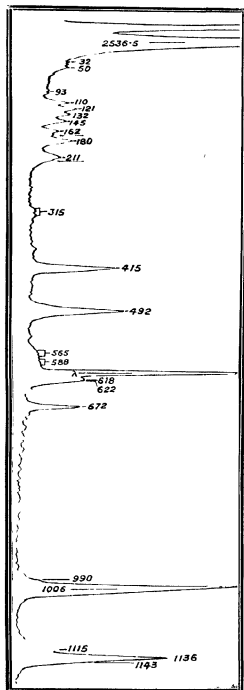
Fig. 5

Krishnamurti . *Ind. Journ. Phys.*, 1930, **5**, 183.

Rasetti . *Nuovo Cimento, Rivista*, 1931, **8**, 89 ; 1932, **9**, 72

Schæfer, Matossi and Aderhold *Phys Zeits.*, 1930b, **31**, 801 ; *Zeits f. Phys.*, 1930c, **65**, 319

Nisi . *Japanese Journ. Phys.*, 1931, **7**, 1.

Cabannes . *Compt rend.*, 1932, **195**, 1353 ; 1938, **207**, 700.

*Aynard . *Ibid.*, 1940, **211**, 647.

Roop Kishore .. *Proc. Ind. Acad Sci.*, A, 1942, **16**, 36

*Cabannes and Aynard . *Journ de Physique*, 1942, **3**, 137

Saksena . *Proc Ind Acad Sci.*, A, 1941, **13**, 25

Rao, D. A. A. S. N *Ibid.*, 1941, **13**, 137.

Rousset and Lochet . *Journ. de Physique*, 1945, **6**, 57

2 *General*

Krishnan, R S *Proc Ind. Acad Sci.*, A, 1945, **22**, 182

Wooster, W. A. *Zeits. f Kristallographie*, 1936, **94**, 375.

Bhagavantam, S. *Proc Ind Acad Sci*, A, 1938, **8**, 345

Hibben *The Raman Effect and Its Chemical Applications*, 1939

3 *Water of Crystallisation*

Nisi *Japanese Journ Phys*, 1931, **7**, 1

Ananthakrishnan *Proc Ind Acad Sci*, A, 1937, **5**, 447

Hibben . *Journ Chem Phys*, 1937, **5**, 166.

Canals and Peyrot *Compt rend.*, 1938, **207**, 224.

Nayar *Proc. Ind Acad Sci*, A, 1938, **8**, 419.

Lakshman Rao . *Ibid*, 1941, **14**, 48

4 *Infra-red*

Kock, J. . *Ann. der Phys*, 1908, **26**, 974

Coblentz . *Phys Rev*, 1910, **30**, 322 , *Bull Bur. Stds*, 1911, **7**, 619

Schæfer and Schubert , *Ann der Phys.*, 1916, **50**, 283.

* The author could not refer to the original papers as the relevant journals have not been received in India. The results were taken from the American *Chemical Abstracts*.

DESCRIPTION OF PLATES

Fig. 1. (a) The complete Raman spectrum of gypsum taken with E3 spectrograph (b) Comparison spectrum of the mercury arc.

Fig 2. (a) Spectrum of the mercury arc (b) The lattice spectrum of gypsum taken with the same instrument but using a finer slit and an efficient mercury vapour filter (c) Its microphotometric record

Fig 3. The microphotometric record of the high frequency water bands

Fig. 4. The spectrum of gypsum showing the lattice lines and the lines due to the SO₄ ion, taken with the E1 spectrograph

Fig. 5. Its microphotometric record.

EGG-YOLK PROTEINS OF *ARIUS JELLA*

By M. DAMODARAN AND K. RAMAMURTI

(From the University Biochemical Laboratory, Madras)

PROTEINS of egg-yolk are of interest not only from the nutritional point of view but also from that of chemical embryology. The main protein of fish egg-yolk belongs to the group of 'ichthulins' which are globulins containing phosphorus and are analogous in properties to the vitellins of avian yolk. Needham (1929) working with the egg-yolk of the Selachian came to the conclusion that the analogy between the proteins of avian and fish egg-yolk extends further and that Selachian yolk contains in addition to the ichthulin, a pseudoglobulin corresponding to the livetin of avian egg. In the present investigation two new proteins have been isolated from the egg-yolk of *Arius Jella* (cat-fish). While one of these, the main constituent, is a typical ichthulin, the second protein conformed in properties to an albumin and not a pseudoglobulin.

The eggs of *Arius Jella* are readily available in Madras being found deposited in bunches on the mud of the brackish waters on the coast. They were made available to us by the kindness of Prof. R. Gopala Aiyar of the Zoology Department of this University. The eggs were brought to the Laboratory after collection immersed in brackish water. After rinsing off the latter, the yolk was liberated by puncturing through the vitelline membrane with a thick needle and collected in a beaker placed in ice. The amount of yolk from 100 eggs—individual eggs measure from 9 mm. to 12 mm. in diameter—was usually about 80 g., and had a volume of about 70 ml As determined by precipitation with trichloracetic acid the non-protein nitrogen amounted to 4·83% of the total nitrogen.

PREPARATION OF THE ICHTHULIN

The yolk was mixed with ten volumes of distilled water and while kept at 0° C. stirred vigorously for two hours by a mechanical stirrer. This procedure was sufficient to bring down the ichthulin which separated out as a slimy precipitate with the colour and consistency of thick cream. The supernatant liquid (A) was preserved in the ice-chest for the next stage. The precipitate was washed with ice-cold water and then dissolved in the minimal volume of 10% sodium chloride solution necessary. After filtration

through paper pulp the clear filtrate which had a pH of 6·5, was diluted with vigorous stirring with 15 times the volume of distilled water when rapid precipitation of the protein took place. After allowing to settle overnight in the ice-chest, the precipitate was separated by centrifuging, redissolved in the minimum amount of 10% sodium chloride, filtered again through pulp and reprecipitated by dilution as before. This was repeated four times, a small portion of the precipitate obtained each time being washed free from chloride with water at 0° C. and dehydrated with acetone and, after drying over phosphorous pentoxide *in vacuo* at 100° C., used for nitrogen determination. The nitrogen content (% of dry weight) after successive precipitations was 16·98, 16 82 and 16·83 respectively, the values remaining unchanged after the third precipitation. The phosphorus present in various preparations ranged from 0 41 to 0·39%. The yield of the globulin was 25 g per 100 g. of yolk.

PREPARATION OF THE ALBUMIN

The supernatant liquid (A) was filtered through drill to remove traces of the first precipitate. No precipitate was obtained on half saturation with ammonium sulphate indicating complete absence of globulin or pseudoglobulin. On fully saturating with ammonium sulphate, a white flocculent precipitate was formed which floated upon the surface of the liquid. This was separated by filtration through fluted filter-paper, the precipitate collected from the filter-paper with a horn spatula while still moist and dissolved in a small quantity of distilled water. The solution was filtered through a small pad of paper pulp and the protein again precipitated, by saturation with ammonium sulphate. This precipitate was redissolved in distilled water and the solution dialysed against distilled water in cellophane in a 'Schnell' dialyser till free from sulphate. The protein was precipitated out by the addition of acetone, washed in the centrifuge glass with graded strengths of acetone, and dried *in vacuo* over sulphuric acid. The nitrogen content of the albumin was 14·57%, the yield of the protein being 10 g. for 100 g. of yolk.

ANALYSES OF THE PROTEINS

The following analyses were carried out on the two proteins thus prepared:

(1) *Phosphorus.*—For determination of phosphorus samples of the proteins after extraction with methyl alcohol, acetone, petroleum ether and ether in succession were oxidised with nitric acid and then analysed according to the colorimetric method of Fiske and Subba Rao (1925).

The phosphorus content of the two proteins were: globulin 0·39%, albumin 0·79%, the value for the albumin being higher than for the globulin contrary to previous findings.

(2) Nitrogen distribution by Van Slyke method with the modifications introduced in this Laboratory (Damodaran, 1931; Damodaran and Sivaswami, 1936; Krishnan and Krishnaswamy, 1939).

(3) The basic amino-acids according to Block (1934) as modified by Tristram (1939).

(4) Arginine was determined on a separate hydrolysate by colorimetry (Jorpes and Thoren, 1932), by precipitation as monoflavionate (Vickery, 1940), and by means of arginase (Hunter and Dauphinee, 1930).

(5) Histidine was estimated in the basic fraction by a colorimetric method (Hanke and Koessler, 1920) and also as histidine nitranilate according to Block (1940).

(6) Cystine by the methods of Folin and Marenzi (1929) and Prunty (1933).

(7) Tyrosine and tryptophane were determined according to Folin and Ciocalteu (1927).

Analysis of the Globulin

As % of total N.

Amide	..	.	7·95
Humin	..	..	.. 1·15
Dicarboxylic acids		.	. 11·36
Bases	..	..	.. 24·10
Arginine	..	..	.. 14·48[1], 14·68[2], 14·20[3], 12·95[4], 14·21[5]
Histidine	..		.. 1·25[1], 1·40[6], 1·37[7]
Cystine	.	.	.. 0·85[8], 0·92[9]
Lysine	..	..	. 9·40[1]
Monoamino monocarboxylic acid	..		46·80
Non-amino	..	..	8·50
Tyrosine	.	.	.. 2·02
Tryptophane	..	..	. 1·07

---
[1] Block. [2] Jorpes and Thoren [3] Hunter and Dauphinee. [4] Vickery. [5] Block fraction. Jorpes and Thoren. [6] Block fraction, Hanke and Koessler. [7] Block, Histidine as nitranilate, [8] Folin and Marenzi. [9] Prunty.

Analysis of the Albumin

As % of total N.

Amide	..	..	.. 6·77
Humin	..	..	. 0·89
Dicarboxylic acids	..	..	12·35
Bases	..	..	.. 26·48
Arginine	..	..	.. 14 87[1], 14·97[2], 14·60[3], 12·72[1], 15·43[5]
Histidine	..	..	. 1 87[1], 1 90[1]
Lysine	..	.	.. 9 74
Monoamino monocarboxylic acid	..	47·10
Non-amino	..	..	. 7·07
Tyrosine	..	.	2·80
Tryptophane	..	.	0 72

[1] Block. [2] Jorpes and Thoren. [3] Hunter and Dauphinee. [4] Vickery [5] Block fraction, Jorpes and Thoren [6] Block fraction, Hanke and Koessler

SUMMARY

The egg-yolk of *Arius Jella* has been shown to consist of two proteins, an ichthulin of the usual type and an albumin, a class of protein not hitherto found in fish eggs.

The two proteins have been isolated in the pure state and analysed for their content of the more important amino-acids.

REFERENCES

Block, R. J.   *J. biol chem*, 1934, **106**, 457.
————   *Ibid*, 1940, **133**, 67
Damodaran, M   *Biochem J*, 1931, **25**, 190
———— and Sivaswamy, T G   *Ibid*, 1936, 30, 604
Folin, O, and Ciocalteu, V   *J biol chem*, 1927, **73**, 627
———— and Marenzi, A D   . *Ibid*, 1929, **83**, 103.
Fiske and Subba Rao   *Ibid*, 1925, **66**, 375.
Hanke M T., and Koesller, K K *Ibid*, 1920, **43**, 527.
Hunter, A, and Dauphinee, J A   *Ibid*, 1930, 85, 627.
Jorpes, E, and Thoren, S.   . *Biochem J.*, 1932, **26**, 1505.
Krishnan, P S, and Krishna-   *Ibid*, 1939, 33, 1284.
   swamy, T. K.
Needham, J.   *Ibid.*, 1929, **23**, 1223.
Prunty, F. T G.   . *Ibid.*, 1933, **27**, 387
Tristram, G. R.   . *Ibid.*, 1939, 33, 1271.
Vickery, H B   *J. biol. chem*, 1940, **132**, 325.

A8

THE WAXY MATTER OF THE FLOWERS OF *HIBISCUS SABDARIFFA* AND *CARTHAMUS TINCTORIUS*

By P. Bhaskara Rama Murti and T. R. Seshadri

(From the Departments of Chemistry and Chemical Technology, Andhra University)

Only a few cases of wax from flowers seem to have received attention Rose petal wax was studied by Prophete.[1] It contains about 50% of hydrocarbons and the results suggest that paraffins of chain length shorter than C_{25} and possibly olefines are present Amongst the constituents of the flowers of *Arnica Montana* was found the substance Arnidendiol having the formula $C_{30}H_{50}O_2$.[2] This probably belongs to the triterpene group. Paraffins were isolated from the flowers of *Tagetes grandiflora* by Kuhn *et al.*[3] The mixture melted at 68 5° to 69 5° and was considered to be made up of the C_{31} compound with a small amount of the higher homologue (C_{33}). The wax components of the flowers of *Butea frondosa*[4] and *Pongamia glabra*[5] have recently been examined by Murti *et al* The former seems to consist entirely of wax esters whereas the latter consists predominantly of these esters along with minor quantities of paraffins.

Small quantities of the waxy matter of the flowers of *Hibiscus sabdariffa* and *Carthamus tinctorius* were obtained as by-products in the course of the study of their pigments The results of their chemical examination are given below. Both of these waxes consisted predominantly of hydrocarbons

Hibiscus sabdariffa.—

This plant belongs to the family Malvaceæ. The dry petals were repeatedly extracted with boiling alcohol. On concentrating the alcohol extract and allowing it to stand for several weeks hibiscitrin separated out along with some quantity of wax. Subsequently the clear alcoholic solution was thrown into a large excess of boiling water whereby most of the colouring matter went into solution and the insoluble sticky solid contained the main part of the wax and some resin. About 30 grams of this material was available. As much colouring matter as possible was again removed by repeatedly boiling the solid with water. By subsequently extracting it with ether, it was separated into the ether-insoluble portion (A) and the ether-soluble portion (B).

*Fraction (A): Phytosterolin —*The light brown solid (3·0g.) thus obtained melted at about 230°. It was found to be insoluble in water and the

289

P. Bhaskara Rama Murti and T. R. Seshadri

ordinary organic solvents, but it dissolved in hot glacial acetic acid and in pyridine. The clear solution in acetic acid, on gradual dilution with water, deposited a crystalline solid which after one more crystallisation from the above solvent yielded the compound in the form of hexagonal plates melting at 251–52° (decomp.). With the Liebermann-Burchard reagent it produced a play of colours, pink-blue-green and with the Salkowski reagent the chloroform layer assumed a blood red colour while the sulphuric acid layer exhibited a powerful green fluorescence. The high melting point and the colour reactions coupled with the sparing solubility of the compound in the ordinary solvents indicated the possibility of its being a glycoside of a sterol. (Found in a sample dried at 130°. C, 72·4; H, 10·2; $C_{35}H_{60}O_6$ requires C, 72·9 and H, 10·4%.).

The sterolin (0·2 g.) was dissolved in amyl alcohol (25 c.c.), hydrochloric acid (2 c.c.) added and the mixture boiled under reflux for 5 hours. After removing the solvent by steam distillation, the products of hydrolysis were taken up with water and ether-extracted. The ether solution was washed with water, dried over anhydrous sodium sulphate and distilled to remove the solvent completely. The residue on crystallisation from alcohol was in the form of colourless needles and it responded to the usual sterol colour reactions. It melted at 136–37°. (Found: C, 83·8; H, 12·2; $C_{29}H_{50}O$ requires C, 84·1; H, 12·1%.) $[\alpha]_D^{30°}$, – 35·0° in chloroform solution. The crystalline sterol (0·12 g.) was boiled with acetic anhydride in presence of sodium acetate for three hours. The resulting acetate, on crystallisation from alcohol, was obtained in the form of colourless needles and melted at 126–27°. (Found: C, 81·4; H, 11·4; $C_{31}H_{52}O_2$ requires C, 81·6; H, 11·4%.) $[\alpha]_D^{30°}$, – 20·0° in chloroform solution. The above properties are characteristic of sitosterol. The presence of a reducing sugar was detected in the aqueous acid solution by testing it with Fehling's solution and its identity with glucose was established by preparing its osazone.

Fraction (B).—The ether solution was still contaminated with some flavonols and they were removed by repeated extraction with aqueous sodium hydroxide. The wax recovered from the ether solution had a low and indefinite melting point. It could not be purified by simple crystallisation from any solvent; hence it was subjected to saponification using boiling alcoholic potash. The acid portion was negligible indicating that the wax consisted almost completely of unsaponifiable matter. When the unsaponifiable matter (12·5 g.) was crystallised from benzene-alcohol mixture a colourless product (10·0 g.) was easily obtained. Analysis for carbon and hydrogen indicated that it consisted of hydrocarbons. It was

easily soluble in cold petroleum and was purified by extraction with this solvent. To effect further purification, it was dissolved in hot amyl alcohol followed by the addition of concentrated hydrochloric acid and the contents were boiled for a few minutes On gradual cooling a cake of hydrocarbons was formed on the top of the liquid and was carefully removed. Subsequently it was boiled with acetic anhydride in the presence of sodium acetate and again it was purified by treatment with sulpuric acid at 130°; during the last process no blackening was noticed. Finally on crystallisation from alcohol and then from petroleum ether, it was obtained as glistening crystals (rhombs) It then melted sharp at 59° and the melt solidified at 58·5°. (Found: C, 84·9; H, 14·8%.). Its melting point corresponds to an average chain length of $C_{27·3}$ on the curve establishing the relationship between the melting points and the chain lengths of hydrocarbons.[6] Hence it was considered to be composed predominantly of C_{27} — hydrocarbons.

When the benzene-alcohol mother liquor was evaporated, the residue gave tests for sterols. But it could not be purified by simple crystallisation Hence it was acetylated by boiling with acetic anhydride and a few drops of pyridine. After diluting the mixture with water and allowing the product to stand, it was ether extracted. The solvent was evaporated and the residue crystallised from methyl and ethyl alcohols in succession. Finally the substance was obtained as colourless needles melting at 126–27°. It agreed in all properties with the sitosterol acetate obtained earlier from the phytosterolin and their mixed melting point was undepressed. On saponification by boiling with alcoholic potash the free sterol was obtained and it was found to be identical with the sitosterol sample obtained by the hydrolysis of the phytosterolin, the mixed melting point being again undepressed.

Carthamus tinctorius (Safflower):—

The sample of the flower petals (4·0 kg.) was obtained from Bellary in the Deccan Plateau. The wax was isolated from the flower petals by means of carbon tetrachloride. It was contaminated with some essential oil and also some colouring matter. The latter was removed by extracting the carbon tetrachloride solution with aqueous alkali. After removing the solvent the residue (15·0 g.) was first subjected to steam distillation in order to remove the essential oil and then to saponification by boiling its benzene solution with alcoholic potash.

Unsaponifiable matter.—This (13·0 g.) was obtained as an yellow solid and it melted indefinitely at about 50° It readily dissolved in chloroform, benzene and petroleum ether and sparingly in methyl and ethyl alcohols.

To resolve it into different fractions tests were made using various mixtures of solvents. The following method was found satisfactory. The material was dissolved in chloroform (150 c.c.), an equal amount of alcohol added and the contents were stirred. On allowing to stand for some time a colourless shining solid began to separate out. It was filtered and washed with alcohol in order to remove coloured impurities. It then appeared as rhombs under the microscope and melted at 62–64°. With the Liebermann-Burchard reagent no colour was produced indicating the complete absence of sterols and related compounds. It was purified by repeated crystallisation from ether-alcohol mixture. Finally a solid melting at 64° was obtained. Analysis for carbon and hydrogen showed that it was made up almost completely of hydrocarbons. Further purification was effected adopting the method described under *Hibiscus sabdariffa* followed by treatment with sulphuric acid at 130°. Finally it was crystallised from alcohol and was then obtained as a shining crystalline product which melted at 65° and set at 64·5° (Found: C, 84·8; H, 15·4%) Using the curve establishing the relationship between the melting points and chain lengths its average chain length was found to be C$_{29.5}$. Hence the mixture may be considered to consist mostly of C$_{29}$ and C$_{31}$ hydrocarbons.

The soap left after the removal of the unsaponifiable matter was decomposed by boiling with dilute hydrochloric acid. A mixture of fatty acids melting round about 53° was thus obtained in a small amount. Its neutralisation equivalent was 289·6 It was, therefore, considered to be a mixture of stearic acid and its near homologues probably arising out of the fatty oil contained in the wax.

SUMMARY

The waxy matter isolated from the flowers of *Hibiscus sabdariffa* by alcohol extraction yielded phytosterolin as the ether-insoluble component. The ether-soluble portion consisted mainly of hydrocarbons having chain lengths round about C$_{27}$ along with very small amounts of sitosterol. By the extraction of safflower with carbon tetrachloride was obtained a wax made up mostly of paraffin of chain length C$_{29}$ and near homologues.

REFERENCES

1	Prophetic	Bull. Soc. Chim., 1926, **39**, 600.
2. Dieterle and Engelhard	.	Arch. Pharm., 1940, **278**, 225–35.
3. Kuhn et al.	.	Zeit. Physiol. Chem., 1931, **197**, 152.
4	Murti et al	.	Proc. Ind. Acad. Sci., A, 1940, **12**, 472.
5	——— and Seshadri	Ibid., 1944, **20**, 279.
6	Piper et al	Biochem. J., 1931, **25**, 2082.

NON-OCCURRENCE OF THE *LIGHT-EFFECT* IN HIGH FREQUENCY CONDUCTION AT LOW POTENTIALS

BY S. S. JOSHI AND K. Z. LAD*

(*Chemistry Department, Benares Hindu University*)

FOLLOWING the discovery of the above phenomenon (Joshi, 1939; 1943)· *viz.,* Δ *i* an instantaneous and reversible current decrease on irradiation even in the visible, in chlorine and some other gases, were observations of the discharge current *i* made with various current indicators (Joshi, 1945) and especially a cathode-ray oscillograph (Joshi, 1943; 1944); and of the marked influence on *i* of introducing H.F. and L.F. filters in the current circuit (Joshi, 1945). It was found that, in general, at a constant applied potential *V* and frequency of the A.C. supply *n*, the current *i* contains a large number of frequencies of varying strength in addition to *n*; and that the seat of the *light-effect* lies predominantly in the high frequency components of *i* (Joshi, 1944; 1945). Oscillographic records of *i* obtained under a wide range of conditions have shown that the amplitudes of the high frequency components diminish with but a negligible time-lag, when the system is exposed to light (Joshi, 1944). In view of the significance of these observations from the standpoint of the mechanism of this *light-effect,* it was of interest to investigate this phenomenon when the system is fed with high frequency currents.

A modified Hartley type oscillator was used for generating the high frequency currents. Fig. 1 indicates the general experimental arrangement and the circuit. This consisted essentially of a 415 Philips Triode which was connected on one side to the H.F. choke and one 0·01 μF anode blocking condenser; H.F. grid coil and 0·0002 μF tuning condenser; 0·0001 μF grid condenser and a 60,000 ohm resistance to serve as a grid leak. A Siemens' tube filled with purified chlorine at 200 mm pressure was introduced in the receiving circuit. The inner electrode of this chlorine tube filled with a salt solution was connected through a 0·0001 μF variable condenser, to the receiving coil mentioned above; the outer electrode represented by another tube also filled with salt solution and in which the

---

Siemens' tube was immersed was connected through a Dublier type stabi-
lising resistance of moderate value to a low resistance Cambridge vacuo-
junction connected to a reflection galvanometer. This arrangement proved
markedly current sensitive, since the deflections of the galvanometer are
proportional to i^2.

The P D. developed across the terminals of the ozoniser denoted by V
in Fig. 1 was determined with a thermionic voltmeter V was kept cons-
tant at 0·94 volt, while the frequency input to the ozoniser was varied by
a variation of the capacity of the tuning condenser shown in Fig. 1. The
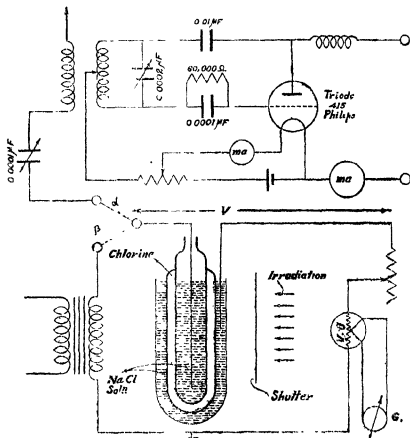
Fig 1

currents flowing through the chlorine tube were observed in dark and under
different radiations at various dial positions of the tuning condenser; these
corresponded to the frequency range of 5 to 12 megacycles per second; as
determined by calibrations made with a wavemeter,

These results have shown that no sensible change of conductivity is caused by light under the conditions described. This is sufficiently illustrated by Table I, which represents but one of the several series of observations made. The current figures are shown within brackets under the corresponding galvanometer deflections, observed in the dark, and when the chlorine tube was exposed to light.

TABLE I

Anode P. D.	..	130 volts
Filament P. D	.	6 ,,
,, Current	.	70 milliamps.
Anode ,,	..	7 ,,
Frequency range	.	5 to 12 megacycles/sec $^{-1}$
Source of irradiation	..	220 volts, 100 watt, (glass) bulb

Dial position of the condenser		0	10	20	30	40	50	60	70
In dark	.	158 (12·6)	250 (15·8)	270 (16·4)	160 (12·64)	15 (3·9)	20 (4·47)	10 (3·16)	30 (5·48)
In light	..	158 (12·6)	250 (15·8)	270 (16·4)	155 (12·45)	15 (3·9)	20 (4·47)	10 (3·16)	30 (5·48)

A series of experiments was next made in which the chlorine tube was excited at much larger potentials and smaller frequencies. It was disconnected from the oscillator circuit at α and connected at β to one of the secondaries of a high tension transformer, of a capacity 3 KVA and of 40 kV, at 150 volts on the primary at 50 cycles frequency. During these observations the fundamental significance of the 'threshold potential' V_m for discharge reactions in general (Joshi, 1929) and the *light-effect* phenomenon in particular (Joshi, 1944) was noticed. Below V_m, which depends on the various operative conditions such as the temperature, inter-electrode distance, the gas pressure and especially the frequency, neither any of the discharge reactions nor the *light-effect* is detected (Joshi, 1944). At 50 cycles frequency, V_m for the above chlorine tube was about 6 kV; below this no *light-effect* was observed despite exposure to intense radiations. Above 6 kV, at each of the galvanometer deflections cited in Table I, obtained by adjustment of the applied potential V, occurrence of the *light-effect* was appreciable. Thus, for example, an application of 9·6 kV to the chlorine tube produced a deflection of 235 units; this diminished instantaneously to 160, corresponding to a *light-effect* of 18 per cent. It is interesting that when the same deflection was obtained with 500 cycles frequency by applying 7 kV, the corresponding *light-effect* was 12 per cent. in agreement with an earlier result (Joshi, 1944).

It is suggested that when the chlorine tube was fed with high frequency currents, the intensity of the corresponding electric field was so low that the system functioned as a capacity only, and that the chief determinant of the *light-effect* phenomenon is a large enough field to produce ionisation by collision of the gas in the annular space   Furthermore, the *light-effect* predominates in the high frequencies produced under the applied potential and not (necessarily) those input to the system

SUMMARY

No *light-effect* was observed when a chlorine-filled Siemens' tube was fed at low potentials with currents of 5 to 12 megacycles frequency. Over the same current range, however, an instantaneous and reversible *light-effect* corresponding to 18 to 12 per cent current decrease at 50 to 500 cycles frequency, and 9·6 to 7 kV applied potential respectively, was produced by light from an incandescent bulb. Fields large enough to cause ionisation by collision of the irradiated gas are considered to be a necessary condition for the production of the phenomenon

REFERENCES

1.	Joshi	*Curr. Sci.*, 1939, **8**, 548
2	————————	. Presidential Address, *Chem Sec*, *Indian Sci Cong*, 1943
3	————————	. *Benares Hindu Univ. J*, 1943, **8**, 99 ; *Nature*, 1944, **154**, 147 , *Curr Sci.*, 1944, **13**, 253.
4	————— ----	*Curr Sci*, 1945, **14**, 67
5	————————	*Trans Faraday Soc*, 1929, **25**, 139 , 1927, **25**, 129

6:7-DIHYDROXY-FLAVONOLS: PART II

By K. Visweswara Rao, L. Ramachandra Row

AND

T. R. Seshadri

(From the Department of Chemistry, Andhra University)

IN Part I[1] was described the preparation of 3·6:7:3′:4′-pentahydroxy-flavone using the following series of reactions:
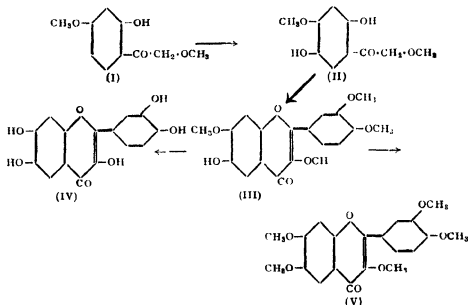
Following the same procedure and using the sodium salts and anhydrides of benzoic, anisic and trimethyl gallic acids for condensation with the ketone (II), the other flavonols of the series with 0, 1 and 3 hydroxyl groups in the side-phenyl nucleus have now been prepared and their properties and those of their derivatives are described in this paper. Certain interesting similarities and gradations in properties have been observed among them and they are discussed below.

Those corresponding to (III) having one free hydroxyl group in position 6, are soluble in aqueous alkali giving stable yellow coloured solutions. Their alcoholic solutions exhibit greenish blue fluorescence and give only

297

a feeble colour with ferric chloride. There is decreasing intensity in the colour of the solid substance with increasing number of methoxyls in the side-phenyl nucleus. 3 : 7 : 4'-Trimethoxy-6-hydroxy flavone is bright yellow in colour, the next higher member only pale yellow and the last member is quite colourless.

The poly-hydroxy compounds corresponding to (IV) are pale yellow substances sparingly soluble in alcohol. Their alcoholic solutions exhibit bright green fluorescence and give deep greenish brown colour with ferric chloride. The colour changes exhibited by the earlier members in solutions of alkaline pH are not prominent; but the highest member quickly changes its colour in dilute alkali from yellow to pink, violet, blue and finally brown. They all exhibit bright bluish green fluorescence in concentrated sulphuric acid

Among the completely methylated compounds (Type V) the hexa- and penta-methoxy flavones exhibit pale blue fluorescence in alcoholic solution, but the lower members do not. However, all of them give bright bluish-green fluorescence in concentrated sulphuric acid solution.

An alternative method of preparing the above-mentioned 6 : 7-dihydroxy-flavonols would be to start with hydroxy-quinol and proceed as indicated below:

(VII)   (VIII)
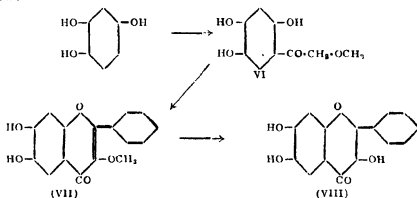
6 : 7-Dihydroxy-flavone [2,3] itself was prepared in the past by a similar pro-cedure employing 2 : 4 : 5-tri-hydroxy acetophenone or its methyl ether. There has been some difference of opinion regarding the exact constitution of the ketone obtained from hydroxy-quinol Chada and Venkatraman[3] have given satisfactory arguments in support of its constitution as 2 : 4 : 5-tri-hydroxy-acetophenone. Based on similar considerations the product of the condensation of methoxy acetonitrile with hydroxy-quinol should have the constitution (VI). This has now been independently supported by

methylating the compound completely and comparing the resulting product with w : 2 : 4 : 5-tetra-methoxy-aceto-phenone prepared by Row and Seshadri[1] by a different method. The two ketones are found to be identical. The preparation of the ω-methoxy-ketone (VI) was first made by Healy and Robinson[4] who converted it into 2-methyl-3-methoxy-6 : 7-dihydroxy-chromone. The ketone normally comes as a monohydrate and melts low; the anhydrous substance melts at 150°

Though the second method given above may look simpler, there are difficulties of experimental technique particularly in regard to the preparation of pure samples of hydroxy-quinol and of its conversion into the ω-methoxy-ketone (VI). Attempts to simplify the synthesis by using the more easily available triacetate of hydroxy-quinol were not successful. The acetate does not undergo deacetylation or condensation with acetonitrile under the conditions of Hoesch reaction. Consequently the earlier method adopted by Row and Seshadri for preparing these flavonols seems to be more convenient

<div align="center">EXPERIMENTAL</div>

ω-Methoxy-2 : 4 . 5-trihydroxy-acetophenone (VI):—As reported by Healy and Robinson[4] the yield of this ketone is very low under the ordinary conditions of Hoesch reaction. Even under these conditions it could be raised to about 30% by employing purified hydroxy-quinol and hydrolysing the ketimine hydrochloride in an atmosphere of carbon dioxide. The product is a coloured oil which does not solidify and could not be crystallised directly. But on treatment with saturated sodium bisulphite solution it rapidly turns into a mass of crystals (colourless needles) and can be subsequently crystallised from acetone or acetone-benzene mixture. It first comes as a monohydrate and melts at 110–11°; but crystallisation from anhydrous acetone-benzene mixture yields the anhydrous form melting at 150–51°. (Found: C, 54·3; H, 4·9, $C_9H_{10}O_5$ requires C, 54·5; H, 5·1%.)

ω : 2 · 4 . 5-Tetramethoxy-acetophenone.—ω-Methoxy-2 : 4 : 5-trihydroxy-acetophenone (VI) (0·15 g.) was dissolved in dry acetone (25 c.c.) and treated with dimethyl sulphate (0·5 c.c.) and anhydrous potassium carbonate (1 g.). The mixture was refluxed for 12 hours. After removing the acetone, water was added to dissolve the potassium salts and the mixture extracted with ether. The ether solution was shaken with aqueous alkali to remove any partially methylated ketone It was then washed with water and evaporated; a colourless crystalline solid was obtained and it was purified by crystallising twice from alcohol It came out as colourless, long, transparent rectangular plates melting at 133–34°. It was insoluble in alkali and gave no colour with ferric chloride. Mixed melting point with

the substance prepared by methylating ω : 4-dimethoxy-2 : 5-dihydroxy acetophenone by Row and Seshadri was not depressed. (Found: C, 60·0; H, 6·9; $C_{12}H_{16}O_5$ requires C, 60·0 and H, 6·7%.)

6 : 7-Dihydroxy-3-methoxy-flavone (VII):—An intimate mixture of ω-methoxy-2 : 4 : 5-tri-hydroxy-acetophenone (VI) (0·9 g.), benzoic anhydride (9 g.) and sodium benzoate (4 g.) was heated *in vacuo* at 170–80° in an oil-bath for four hours. The pale brown solid was broken up with a glass-rod and refluxed with alcohol (25 c.c.) for 10 minutes. Alcoholic potash (8 g. of potash in 55 c.c.) was slowly introduced through the condenser and the refluxing continued for 20 minutes more. The solvent was then distilled under reduced pressure keeping the temperature as low as possible. Water (40 c.c.) was added to the residue and the clear solution obtained was saturated with carbon dioxide when a brown solid separated out. It was filtered and washed with water. The filtrate was repeatedly extracted with ether (5 times) and some more substance recovered by evaporating the ethereal extract. The two lots were combined and purified by crystallisation from alcohol. Two crystallisations were found sufficient to give the compound in a state of purity. 6 : 7-Dihydroxy-3-methoxy-flavone was thus obtained in the form of very pale yellow rectangular plates melting at 242–44°. With alcoholic ferric chloride it gave an olive green colour. It readily dissolved in alkali forming a bright yellow solution. In concentrated sulphuric acid, an yellow solution with blue fluorescence was obtained. Yield 0·45 g. (Found: C, 68·0; H, 4·2; $C_{16}H_{12}O_5$ requires C, 67·6 and H, 4·2%.)

3 : 6 : 7-Trimethoxy-flavone·   First Method:—6 : 7-Dihydroxy-3-methoxy flavone (VII) (0·1 g.) was treated with dimethyl sulphate (0·5 c.c.) and anhydrous potassium carbonate (1 g.) in anhydrous acetone (25 c.c.) After refluxing the mixture for 12 hours, the solvent was removed by evaporation, the residue treated with water and the mixture extracted twice with ether. The ether extract was first shaken with a weak solution of alkali and then twice with water. It was then evaporated to dryness and the colourless crystalline solid thus obtained, was crystallised from alcohol The trimethoxy flavone crystallised in the form of colourless long needles melting at 175–76°. It gave no colour with ferric chloride in alcoholic solution and was insoluble in alkali (Found: C, 69·2; H, 4·7; $C_{18}H_{16}O_5$ requires C, 69·2 and H. 5·0%.)

Second   Method.—ω : 4-Dimethoxy-2 : 5-dihydroxy-acetophenone (II) (0·25 g.) was condensed with benzoic anhydride (2·0 g.) and sodium benzoate (0·5g.) according to the method of Allan and Robinson After hydrolysis, the product was crystallised from alcohol, when 3:7-dimethoxy-6-hydroxy-flavone was obtained in the form of narrow rectangular plates and needles

melting at 198–200°. This was methylated using dimethyl sulphate, anhydrous acetone and anhydrous potassium carbonate as in the first method. The trimethyl ether was crystallised twice from alcohol and obtained in the form of colourless long needles melting at 175–176°. The mixed melting point with the sample from the first method was not depressed.

3 : 6 : 7-Trihydroxy-flavone (VIII):—6 · 7-Dihydroxy-3-methoxy-flavone (VII)(0·3 g.) was dissolved in acetic anhydride (5 c.c.) by warming and the solution treated with hydriodic acid (7 c.c., *d* 1 7) slowly with stirring and cooling in ice water. The solution was then gently boiled under reflux for an hour; water was then added to the cooled solution and the mixture treated with a current of sulphurdioxide. The solid product was filtered and washed well with water It was purified by crystallising twice from alcohol when it was obtained in the form of elongated rectangular prisms It darkened at about 300° and melted completely at 312–315°. Yield 0 2. g. It was sparingly soluble in cold alcohol and the solution exhibited a feeble blue fluorescence. With ferric chloride it gave a dark greenish-brown colour (Found: C, 66 5; H, 3 6, $C_{15}H_{10}O_5$ requires C, 66·7 and H, 3·7%.)

The triacetate of the above flavonol was prepared by refluxing it with acetic anhydride and anhydrous sodium acetate for an hour and a half. It crystallised from alcohol (animal charcoal) in the form of colourless triangular prisms melting at 191–192° (Found: C, 63·6; H, 4·0; $C_{21}H_{16}O_8$ requires C, 63 6 and H, 4 1%.)

3. 7: 4′-Trimethoxy-6-hydroxy-flavone —ω: 4-Dimethoxy-2 : 5-dihydroxy acetophenone (II) was condensed with anisic anhydride (8 g.) and sodium anisate (2 g.) in the usual manner. The product obtained after hydrolysis and neutralisation of the alkali with carbon dioxide was purified by crystallisation from glacial acetic acid. It came out in the form of yellow glistening crystals melting at about 220°. A second crystallisation from alcohol gave the pure compound in the form of bright yellow rectangular plates and prisms melting at 225–26°. Yield, 0·9 g. It was sparingly soluble in alcohol; the alcoholic solution exhibited a feeble green fluorescence and did not give any colour with ferric chloride. It was readily soluble in aqueous alkali giving a bright yellow colour. (Found: C, 65·3; H, 4·6; $C_{18}H_{16}O_6$ requires C, 65·9 and H, 4·9%.)

3 : 6 : 7 : 4′-Tetra-methoxy-flavone was obtained by methylating the above flavone with dimethyl sulphate and anhydrous potassium carbonate in anhydrous acetone medium as before. After two crystallisations from alcohol it was obtained as colourless narrow rectangular plates melting at 164–65°. It did not dissolve in alkali and developed no colour with ferric chloride

in alcoholic solution. (Found: C, 66·9; H, 5·7; $C_{19}H_{18}O_6$ requires C, 66·9 and H, 5·3%.)

3 : 6 : 7 : 4'-Tetra-hydroxy-flavones —The demethylation of 3 : 7 : 4'-tri-methoxy-6-hydroxy-flavone was effected with hydriodic acid (d. 1·7) in the usual manner. The product was sparingly soluble in alcohol and acetic acid. It was, however, crystallised from glacial acetic acid-acetone-ethyl acetate mixture from which it came out as yellow thin rectangular plates. It did not melt below 320° and darkened above that temperature. An alcoholic solution of the substance exhibited a greenish blue fluorescence and gave a deep olive green colour with ferric chloride. The substance was readily soluble in dilute alkali giving a bright yellow coloured solution. (Found: C, 59·3; H, 3·5; $C_{15}H_{10}O_6$, H_2O requires C, 59·2 and H, 3·9%.)

The tetra-hydroxy-flavone was acetylated using acetic anhydride and sodium acetate The acetate crystallised from alcohol in the form of thin rectangular plates melting at 193–95° (Found: C, 60·6; H, 3·7; $C_{23}H_{18}O_{10}$ requires C, 60·8 and H, 4 0%.)

3 : 7 : 3' : 4' 5'-Pentamethoxy-6-hydroxy-flavone —ω. 4-Dimethoxy-2 : 5-di-hydroxy-acetophenone (II) (1 g.) was condensed in the usual manner with O-trimethyl gallic anhydride (12 g.) and sodium O-trimethyl gallate (4 g.). The condensation product was collected after hydrolysis and neutralisa-tion of the alkali with carbon dioxide and was crystallised from alcohol. It was obtained in the form of colourless narrow, rectangular prisms melting at 203–04°. Yield, 0·8 g. It was easily soluble in alcohol and gave no characteristic colour with ferric chloride In aqueous sodium hydroxide it dissolved readily forming an yellow coloured solution. (Found: C, 62·1; H, 5·4; $C_{20}H_{20}O_8$ requires C, 61·9 and H, 5·2%.)

3:6:7:3':4':5'-Hexamethoxy-flavone was prepared by methylating the above compound with dimethyl sulphate and anhydrous potassium carbo-nate in anhydrous acetone medium. It crystallised from alcohol in the form of broad rectangular plates melting at 204–05° It gave no colour with ferric chloride and did not dissolve in aqueous alkali. It exhibited a blue fluorescence in alcoholic solution The mixed melting point with the 6-hydroxy compound was considerably depressed (180–85°) showing that they were not identical. (Found: C, 62·9; H, 5·5; $C_{21}H_{22}O_8$ requires C, 62·7 and H, 5·5%.)

3 : 6 : 7 : 3' : 4' : 5'-Hexahydroxy-flavone:—The above pentamethoxy-6-hydroxy flavone was demethylated using hydriodic acid (d. 1·7). The yellow solid obtained was sparingly soluble in alcohol, acetic acid, acetone and ethyl acetate. It was crystallised from aqueous pyridine from which it

came out as star-like clusters of needles. It did not melt below 330°. An alcoholic solution of the flavonol exhibited a green fluorescence and developed a dark greenish brown colour with ferric chloride. In dilute aqueous alkali it dissolved readily to give an yellow solution which quickly changed from yellow to pink, violet, blue and finally to brown. (Found: C, 50·7; H, 4·0; $C_{15}H_{10}O_8$, 2 H_2O requires C, 50·9 and H, 4·0%.)

The acetate of the pentahydroxy flavonol was prepared in the usual manner by refluxing the flavonol with acetic anhydride and anhydrous sodium acetate for about an hour and a half. It crystallised from alcohol in the form of silky narrow rectangular plates melting at 227–29°. (Found C, 56·4; H, 4·1; $C_{27}H_{22}O_{14}$ requires C, 56·8 and H, 3·9%.)

SUMMARY

Starting from ω-methoxy-resacetophenone and adopting the procedure described in Part I, 6 : 7-dihydroxy flavonols with 0, 1 and 3 hydroxyls in the side-phenyl nucleus have been prepared. The characteristic properties of the group with reference to the hydroxy-compounds and their partial and complete methyl ethers are described. An alternative method starting with hydroxy-quinol has also been investigated and the simplest member of the group prepared by this method also

REFERENCES

1. Row and Seshadri   *Proc Ind. Acad. Sci*, 1945, **21 A**, 155.
2. Reigrodsky and Tambor *Ber.*, 1910, **43**, 1964
3. Chada and Venkataraman *J C S*, 1933, 1073
4. Healy and Robinson   *Ibid*, 1934, 1628

CHEMICAL COMPOSITION OF *CALOTROPIS GIGANTEA*

Part VI. Flowers. A Comparison of the Composition of the Various Parts of the Plant

By P. Bhaskara Rama Murti and T. R. Seshadri

(From the Departments of Chemistry and Chemical Technology, Andhra University)

The flowers are ivory white outside and purple inside and are found all through the year They contain a considerable amount of latex A small quantity of the flowers was collected and examined with a view to see if they contain any special components and in a general way to effect comparison between these and the other parts of the plant. They could also be taken as representative flowers of the natural order Asclepiadaceæ

The waxy matter of the flowers was extracted by means of ligroin. By careful fractionation it could be separated into two main fractions, one of which contained resinols and sterols as esters and the other consisted mainly of aliphatic components Detailed analysis of the former revealed the presence of α- and β-calotropeols along with β-amyrin. A small amount of sterol could also be obtained. These were present as esters of volatile as well as non-volatile fatty acids. The aliphatic waxy matter seemed to consist almost entirely of esters derived from C_{34} alcohol and near homologues and acids of C_{28} and C_{30} dimensions There were only small amounts of free acids.

The subsequent extraction with alcohol of the fat-free flowers yielded only mineral salts such as citrates and chlorides of sodium and potassium

EXPERIMENTAL

The flowers of *Calotropis gigantea* were collected fresh in the month of September, the stalks were carefully removed and the remaining portions dried in the sun. The dry flower powder (1·0 kg.) was extracted in a continuous extractor with ligroin and alcohol in succession

Ligroin extract:—The solvent was removed by distillation and the residue (15·0 g.) was dried in the steam oven. It was yellow in colour and waxy to the touch. For purposes of fractionation it was boiled with alcohol (400 c.c.) twice, the clear supernatant liquor was decanted off at about 60°

304

after each extraction and the solutions were mixed together The sticky alcohol-insoluble portion (A) (6·0 g.) melted at about 50° and appeared to be a mixture of esters of resinols with solid fatty acids. The alcoholic solution (B) was concentrated to three-fourths of its bulk by distillation and was allowed to stand overnight A pale yellow solid melting indefinitely between 120° and 150° separated out and on examination was found to be a mixture of aliphatic compounds and resinol derivatives The above conclusion regarding the general nature of the components was arrived at after examining the solid with the Liebermann-Burchard and Salkowski reagents. In the former test a very turbid pink solution was produced and in the latter reaction a clean white solid slowly began to separate out indicating the presence of aliphatic wax. To effect the separation of these two types of components, the solid was again dissolved in alcohol and the solution allowed to cool slowly. The fraction that separated out melted at 80–120° and it was further purified by crystallisation from ethyl acetate. Finally after one more crystallisation from a mixture of acetone and ether (1 : 1) a resinol-free substance (B₁) melting at 88° was obtained. The original alcoholic mother-liquor of (B) obtained from the mixed components and the subsequent mother-liquors collected from (B₁), on further examination, yielded esters of resinols (B₂) melting indefinitely at about 200°. Its low yield did not permit of its individual study and hence (B₂) was added on to (A) and studied along with it.

*Fraction (A + B₂) (Resinols and Sterols):—*The total solid (10 g.) was dissolved in benzene (200 c.c.), N/2 alcoholic potash (500 c.c.) added and the contents were boiled under reflux for 15 hours. Then the major bulk of the solvents was removed and the concentrate was transferred to an open basin and mixed with pumice stone. The contents were rapidly dried and the dry mass was extracted in a Soxhlet extractor with dry acetone The solvent was removed and the residue was dissolved in ether (500 c.c.) The ether solution was thoroughly washed with water in order to render it free of alkali and soap Then the solvent was completely removed by distillation and the residue (6·0 g.) was dissolved in boiling alcohol (200 c.c.). On concentrating the solution to half its bulk a crystalline substance (C) melting at 165–75° separated out. Further concentration yielded some more of the above solid and both the fractions were mixed together. It produced the usual pink colour with the Liebermann-Burchard reagent and an yellow colour with the Salkowski reagent. The mother-liquors on still further concentration yielded fraction (D).

*Fraction (C) (Resinols):—*The fraction (3·8 g.) was dissolved in acetic anhydride (10 c.c.), pyridine (5 c.c.) added and the contents were boiled under

A2

reflux for $3\frac{1}{2}$ hours. They were then largely diluted with water, allowed to stand for some hours and the resulting solid was filtered. It was dissolved in boiling acetone (200 c.c.) and set aside for a day. A crystalline (indefinite) substance melting at 210° separated out. Two more crystallisations raised the melting point to 248° and the substance was obtained in the form of hexagonal plates. It gave all the colour reactions characteristic of calotropeols and their derivatives. No depression was noted in its mixed melting point with the acetate of α-calotropeol and hence its identity was established. From the mother-liquors on careful manipulation very small quantities of the acetates of β-calotropeol and β-amyrin were obtained.

Fraction (D) (Isolation of Phytosterol) :—Its alcoholic solution was concentrated in stages and the resulting fractions were tested with the Liebermann-Burchard reagent at every stage. Such of those which produced only resinol colour reactions were rejected, the more soluble fractions which gave correct sterol colour reactions (display of colours with Liebermann-Burchard reagent) being collected separately. The fraction (1·5 g.) thus obtained was acetylated by boiling with acetic anhydride in presence of pyridine and the resulting product was ether extracted. The residue obtained after removing the solvent was subjected to repeated crystallisation from ethyl acetate and the top fractions were rejected. This precaution was found necessary in view of the fact that the resinols could not be definitely tested for in the presence of sterols and that there was possibility of the sterols being contaminated with them in the top fractions. From the tail fractions, after crystallisation from alcohol, a sharp melting acetate, m.p. 129°, was obtained in the form of colourless needles It gave the correct reaction of sterols. The acetate (0·2 g.) was saponified by boiling with alcoholic potash; the free sterol thus obtained melted at 132° (Found. C, 8° 9; H, 12 8; $C_{29}H_{48}O$ requires C, 84·0; H, 12·0%.) Probably it is a sitosterol.

The Fatty Acids —After extracting the unsaponifiables, the soap was acidified with sulphuric acid and steam distilled The characteristic smell of isovaleric acid was noticed in the distillate and the presence of acetic acid was detected by testing with lanthanum nitrate. The non-volatile acids were then extracted with ether and the ether solution was dried. On removing the solvent completely by distillation, the acid residue (3 0 g.) melted indefinitely between 40° and 50°. One crystallisation from alcohol raised the melting point to about 67° and the mixture had a mean molecular weight of 388·6 It consisted, therefore, of solid acids with a mean chain length of 26 C atoms.

Fraction (B₁) (Wax).—This was sparingly soluble both in ethyl and methyl alcohols even in the hot, moderately soluble in ether and readily in benzene, petroleum ether and chloroform. It had an acid value of 20·0 indicating that most of it was made up of neutral compounds. To effect saponification, it (3·0 g.) was dissolved in benzene (200 c.c.), 7% alcoholic potash (100 c.c.) was added and the contents were boiled under reflux for 15 hours. Then an alcoholic solution (200 c.c.) of calcium chloride (12 g.) was added and the boiling was continued for two more hours. The solvents were distilled off to half the volume and the resulting solid consisting of calcium soaps and unsaponifiable matter was obtained by filtration. It was extracted thrice with dry acetone to dissolve the unsaponifiable matter and the acetone solutions were combined. The solid (1·2 g.) obtained after removing the solvent was crystallised from chloroform. It melted at 89° and appeared as rhombs under the microscope. Its acetate was prepared by boiling it (1·0 g.) with acetic anhydride (5 c.c.) in presence of pyridine (5 c.c.) for 3½ hours. The resulting mixture was largely diluted with water, cooled in ice and then ether extracted. On concentrating the ether solution a crop of crystals melting at 73–74° was obtained. (Found: C, 80·3; H, 12·9, $C_{38}H_{72}O_2$ requires C, 80·6; H, 13·4%.) The alcohol mixture was considered to have an average chain length of $C_{33·5}$ and seemed to be a mixture of C_{33} and C_{34} alcohols mostly. The calcium soap left after the extraction with acetone was decomposed by boiling with dilute sulphuric acid. The liberated acid (1·3 g.) was crystallised from benzene-alcohol mixture and finally from chloroform. It melted at 87° and had a mean molecular weight of 448·8 and may therefore be a mixture of C_{28} and C_{30} acids.

Alcoholic Extract of the Flowers.—On concentrating the alcoholic extract to half its bulk (400 c.c.) and cooling in ice for some days a crystalline solid mixed with some resin settled down. It was purified by digestion with alcohol and the resin-free residue on examination was found to be a mixture of chlorides and citrates of sodium and potassium. It thus resembled the mineral matter obtained from the stem-bark.

COMPARISON OF THE COMPOSITION OF DIFFERENT PARTS
OF *Calotropis gigantea*

A comparative statement of the composition of the various parts of *Calotropis gigantea* is presented in Table I.

There is marked difference in the occurrence of the aliphatic components in the different parts of the plant.[1] The stem bark contains the greatest percentage of aliphatic wax consisting mostly of a mixture of the free acids of C_{30}–C_{32} dimensions. The remaining portion of it is found to be made

TABLE I

		Stem bark	Latex	Root bark	Flowers
Aliphatic wax components—					
Free Acids	..	Present	Nil	Nil	Nil
Esters	..	Negligible	Nil	Nil	Present
Hydrocarbons	..	Present	Nil	Nil	Nil
Acids derived from resinol esters—					
Steam volatile	..	Present	Present	Present	Present
Solid	..	Present	Nil	Present	Present
Liquid	..	Small amount	Nil	Small amount	Small amount
Resinols—					
$C_{30}H_{50}O$	..	α-Calotropeol	α-Calotropeol	..	α-Calotropeol
		β-Calotropeol	β-Calotropeol	..	β-Calotropeol
		β-Amyrin	β-Amyrin	β-Amyrin	β-Amyrin
$C_{30}H_{50}O_2$	..	Giganteol	Nil	Giganteol and isogiganteol	Nil
Sterols	..	Present	Nil	Present	Present
Cardiac poison	..	Very little	Gigantin present	Small quantities	Very little

up of hydrocarbons, the true esters being negligible in amount. Latex and root bark are conspicuous for the absence of these constituents. The aliphatic waxy portion obtained from the flowers differs from that of the stem bark in consisting mostly of esters to an almost complete exclusion of free acids and hydrocarbons.

On the other hand aliphatic acids occur throughout the plant in combination with resinols as esters. In this respect there is resemblance among the different parts except the latex. Even in the case of the latex, representatives of this type could be found in the volatile acids but the complete absence of both solid and non-volatile liquid fatty acids is noteworthy. The stem bark seems to be the most prolific source for the production of aliphatic components both in variety and in yield. It may be stated here that a similar difference in the composition of the whole plant and of the latex was noted in the case of *Sonchus arvensis* by Stern and Zellner.[2]

Resinols occur all through the plant in the form of esters In the latex they occur as esters of steam volatile acids only, whereas in the other parts esters of both steam volatile and non-volatile higher fatty acids are present. Four resinols are found in the stem bark. Only three of them could be isolated from the latex and flowers. Though the root bark also yields three resinols, it differs sharply from the rest in containing predominantly giganteol and isogiganteol, the latter of which is found to be present only in this part of the plant. The difference is further accentuated by the complete absence in the roots of calotropeols which are evenly distributed throughout the rest of the plant.

Sterols seem to be absent in the latex whereas their presence has been invariably noted in the other parts of the plant. The latex is the best source for the isolation of the cardiac poison of the usharin type. It is present only in minute quantities in the stem bark and in slightly better proportion in the root bark.

SUMMARY

The ligroin extract of the flowers yielded waxy matter. One fraction of it consisted mainly of the esters of the resinols, α- and β-calotropeols and β-amyrin, with volatile as well as long chain fatty acids. There was also some sterol. The non-resinol aliphatic part contained mainly esters of wax acids and alcohols. The alcoholic extract of the wax-free flowers yielded only mineral matter—citrates, chlorides and tartrates of sodium and potassium.

The various parts of *Calotropis gigantea* are compared with regard to the chemical components present in them.

REFERENCES

1	Murti and Seshadri		*Proc. Ind. Acad Sci.*, A, 1943, **18**, 145; 1945, **21**, 8 and 147.
	Balakrishna, Murti and Seshadri		*Ibid*, 1945, **22**, 138
	———. Rajagopalan and Seshadri		*Ibid*, 1945, **22**, 143
2	Stern and Zellner	..	*Monatsh*, 1925, **46**, 459.

CHEMICAL EXAMINATION OF *SOLANUM NIGRUM* LINN.

Part I. The Component Fatty Acids and the Probable Glyceride Structure of the Fatty Oil from Seeds

By Bawa Kartar Singh and Abhay Kumar

(Department of Chemistry, Allahabad University, Allahabad)

[The fatty oil from the seeds of *Solanum nigrum* Linn. has been examined and found to have Sp. Gr. 0·9198 (30° C.); refractive index 1·4712 (25° C.); Acid value 11·62, Sap. value 184·0, Acetyl value 25·7; Hehner value 92·9; unsaponifiable matter 1·4%, R.M value 0·66, Iodine value (Hanus) 123·2; Thiocyanogen value (24 hours) 84·4 The component fatty acids of the oil are Linoleic 46·63%, Oleic 49·73%, Palmitic 1·76%, Stearic 1·88%. The unsaponifiable matter consists of a phytosterol, m.p. 133° C. The component glycerides of the oil are palmitostearo-olein 0·63%, Dipalmito-olein 2·43%, Palmito-oleolinolein 2·48%, Stearo-oleolinolein 3·4%, Oleodilinolein 44·84% and Diolcolinolein 46·22%. The optical rotation could not be found as the oil was too dark to read.]

Solanum nigrum is a small-sized shrub belonging to the natural order, *Solanaceæ* It is distributed throughout India, Ceylon, and all temperate and tropical zones of the world. The chief product of the tree is its fruit, which is spherical and about five millimeters in diameter. It is called 'Chhoti Makoi' in Hindustani. Its English equivalent is 'Black nightshade', 'Hound Berry', etc. The fruit is described as highly medicinal[1, 2, 3] being used as "laxative, alterative, aphrodisiac, tonic, diuretic; improves appetite and taste; useful in diseases of heart and eye, pains, piles, inflammation, 'tridosh', leucoderma, itch, worms in ears, dysentery, hiccough, vomiting, asthma, bronchitis, fever, urinary discharges; improves the voice, favours conception and facilitates delivery; useful in erysipelas and rat-bite, diarrhœa, hydrophobia; mixed with honey it is administered for pulmonary tuberculosis, and with other drugs in snake-bite and scorpion-sting."

An analysis of the oil has been reported by Pendse.[4] He has determined the constants of the oil and also the percentage of the constituent fatty acids. His results differ from ours and are included in Tables I and II for the sake of comparison. The present investigation was undertaken in the first

instance to determine the glyceride structure of the oil as it had not been done so far. We found that the percentage composition of oleic (49 0%) and linoleic (47·22%) acids, as found by us (Tables V and XI) was markedly different from that found by Pendse, *viz.*, oleic acid 68·45% and linoleic acid 25·66%. Further the quantity of solid acids found by Pendse was higher than that found by us. It was therefore, necessary to redetermine the percentage composition of these acids by several methods. Pendse does not describe the locality from which he collected the material; our plants were collected from two villages (Rajapur and Mumfordganj) near Allahabad. A glance at Tables I and II will show that there is a marked difference in our oil and that analysed by Pendse. It may, however, be pointed out that our results, as obtained by different methods, are concordant and, therefore, may be taken as correct.

The investigation has shown the actual number of glycerides to be six whereas the maximum number of individual glycerides, which may be obtained by any combination of four different acids with the glyceryl radical, $CH_2-CH-CH_2$ is forty.
 | | |

Another species of *Solanum*, viz., *S. indicum*, had been previously investigated by one of us for the fatty acid composition and the glyceride structure of oil. The available data of the seed oils of the *Solanaceæ*, which are more abundant than for many other plant families, disclose certain broad features: the seed fat content of palmitic acid is usually between 5 to 10% of the total acids; both oleic and linoleic acids are present in abundance; stearic acid is present in smaller amount than palmitic acid, but other saturated acids are generally absent or present only in very small quantities. In this respect the seed oil of *Solanum nigrum* conforms, in its fatty acid composition, to the abovementioned general type, except that the saturated acids form only about 4% of the total acids, palmitic and stearic acids occurring in equal amounts.

Whereas the fatty acid composition of the oils of *Solanum indicum* and *Solanum nigrum* fairly conforms to the above mentioned type, their glyceride composition, on which the physical and chemical properties depend, is markedly different. They are similar in one respect, *viz.*, the content of oleodilinolein it is 51% in *Solanum indicum* and 45% in *Solanum nigrum*. In other respects there are marked differences not only in the percentage amounts of the glycerides, but also in their nature: the percentage of dioleolinolein is 10·4 in *Solanum indicum* and 46·2 in *Solanum nigrum*; trilinolein occurs to the extent of 1·6% in oil of *Solanum indicum*, but it is absent in that of *Solanum nigrum*.

<div align="center">EXPERIMENTAL</div>

The material employed for this investigation consisted of authentic seeds of *Solanum nigrum* Linn. The preliminary examination of the seeds was conducted and the following results obtained:—

Average weight of seed .	0·0006 gms
Ash content of the seed	7·6%
Water insoluble in ash .	36 69%
Water soluble in ash ..	63·31%

The following is the qualitative composition of ash:—

Water soluble	Sodium, Potassium, Chloride, Carbonate, Sulphate.
Water insoluble .	Calcium, Magnesium, Carbonate, Sulphate.

Fifty gm. of the crushed seeds were extracted in a Soxhlet apparatus with various solvents in succession as given below:—

1	Petroleum ether (40–60°) .	A clear dark green fatty oil was obtained. Yield 21·5%
2.	Absolute ether	A similar product as above Yield 2·64%
3.	Chloroform	A dark green residue. Yield 2 35%
4.	Ethyl acetate	A green residue Yield 2·04%
5	Absolute alchol .	A brown residue Did not give any test for glucoside or sugar. Yield 5·6%
6	70% Alcohol	A similar residue as above. Yield 1·76%

For the purpose of complete examination four kilograms of the seeds were crushed and extracted with petroleum ether (40–60°). It was a dark green transparent clear oil

<div align="center">*Examination of Fatty Oil*</div>

The oil was purified with animal charcoal and Fuller's earth. The physical and chemical constants of the oil were determined as given in Table I.

Five hundred grams of the oil were saponified with alcoholic sodium hydroxide, the unsaponifiable matter removed with ether and the fatty acids liberated. The constants of these mixed fatty acids are given below in Table II.

The mixed fatty acids were then separated into solid and liquid acids by Hilditch's[6] modification of Twitchell's lead salt-alcohol process. The mixed fatty acids (200 gm.) are dissolved in 1000 c.c. of 95% alcohol and

TABLE I

Constants		Present authors' results	Pendse's results
Specific gravity	..	0·9125 (30° C.)	0·8964 (30° C.)
Refractive index		1·4712 (25° C.)	1·4636 (30° C.)
Angle of rotation	.	Oil was too dark to be read	$[\alpha]_D^{28}$ —6·61°
Acid value		11·62	2·4
Saponification value		186·0	184·7
Acetyl value		25·7	9·97
Hehner value	.	92·9	93·1
Unsaponifiable matter	.	1·4%	1·4—1·6%
R.M value		0·66	
Iodine value (Hanus)		123·2	111·7
Thiocyanogen value (24 hours)		84·4	

TABLE II

Constants		Present authors' results	Pendse's results
Neutralization number		200·0	183·4
Saponification Equivalent	..	280·5	305·2
Iodine value (Hanus)		129·0	112·4
Thiocyanogen value (24 hours)		86·6	..

the solution boiled and then mixed with a boiling solution of lead acetate (140 gm.) in 1000 c.c. of 95% alcohol containing 1·5% of glacial acetic acid. The lead salts which are deposited on cooling at 15° C. overnight are recrystallised from two litres of alcohol. The solid acids are regenerated from the crystallised lead salt, and the liquid acids recovered from the lead salts left on evaporation of mixed alcoholic filtrates from both operations. The constants of solid and liquid acids are given in Table III.

TABLE III

Constants		Solid acids	Liquid acids
Percentage		4·37	95·63
Neutralization number	..	201·2	199·4
Saponification equivalent		278·9	281·4
Iodine value (Hanus)		3·73	134·9
Thiocyanogen value (24 hours)	.	2·0	91·5

Examination of Liquid Acids

A known weight of liquid acids was brominated[7,8] in dry ether at —10° C. and kept at this temperature for two hours. No solid separated thus showing the absence of linolenic acid. The excess of bromine was destroyed

with sodium thiosulphate solution, washed with distilled water and dried
over anhydrous sodium sulphate Ether was distilled off. The residue
was dissolved in 500 c.c. of petroleum ether (40–60°) and kept in frigidaire
overnight. Some tetrabromide separated. It was filtered on a weighed
Gooch crucible The filtrate was concentrated to 250 c.c. and again kept
in frigidaire overnight. Some more tetrabromide separated. This also was
filtered into the same Gooch crucible The solvent from filtrate was removed
and the residue (di- and tetrabromide) weighed and the bromine content
of the mixture determined The results of bromination and analysis are
given below in Table IV·

TABLE IV

Weight of acid brominated	2·2696 gm
Weight of linoleic acid tetrabromide .	0·4530 gm
M P of tetrabromide . .	113·0° C
Weight of residue (di-and tetrabromide)	3·7310 gm
Bromine content of residue	44·82%
Weight of linoleic acid tetrabromide in residue	1·8790 gm
Total weight of tetrabromide	2·3320 gm
Weight of oleic acid dibromide in residue	1 8520 gm
Weight of Linoleic acid	1·0880 gm.
Weight of oleic acid ..	1·1820 gm
Percentage of linoleic acid in liquid acid	47·96
Percentage of oleic acid in liquid acids	52·04

Five grams of the mixed acids were oxidized with alkaline permanga-
nate by Bertram's method[9] and 3·84% of solid acids were obtained. This
was repeated with five grams of oil and solid acids thus obtained were 3·48%.

The percentage of linoleic, oleic and solid acids as calculated by differ-
ent methods is given below in Table V.

TABLE V

Method	Oleic acid	Linoleic acid	Solid acids
	%	%	%
1. From thiocyanogen value of mixed acids (Table II)	49·2	47·8	3·0
2. From thiocyanogen value of liquid and solid acids (Table III)	49·82	45·91	4·27
3. By bromination of liquid acids (Table IV)	50·16	46·20	3·64
4. Average of 1 to 3	49·73	46·63	3·64
5. Solid acids by Bertram's method			3·84
6. By glyceride structure (Table XI)	49·00	47·22	3·78
7. Pendse's results .	68·45	25·66	5·89

The percentage weights of the component acids obtained by the differ-
ent methods agree fairly closely amongst themselves as well as with those
deduced from the experiments on the glyceride structure of the oil,

Examination of Solid Acids

The solid acids were converted into methyl esters. 10·52 grams of the esters were fractionally distilled under reduced pressure, and the results of distillation and calculation[10] are given in Tables VI and VII.

TABLE VI

Fraction No	Pressure	Temperature range	Weight in grams
S₁	6 m.m.	175°–180° C	5·295
S₂	6 m.m.	180°–185° C	2·386
S₃	6 m.m.	185°–190° C	1·480
S₄ (residue)			1·149
Total			10·390
Loss			0·280

Fractions S₁ and S₂.—By repeated crystallizations from dilute acetone of the acids liberated
from these fractions gave palmitic acid m.p. 61° C., which was not depressed on adding
an authentic sample of palmitic acid.

Fraction S₃.—On crystallizing from dilute acetone of the liberated acids, stearic acid m.p.
62° C. was obtained. The m.p. was raised by adding an authentic sample of stearic
acid and lowered by palmitic acid

Fraction S₄ (Residue).—The acid was liberated and extracted with petroleum ether and
crystallized from dilute acetone. Stearic acid m.p. 63° C. was obtained which was
raised by adding an authentic sample of stearic acid. The molecular weight was found
to be 282·4

TABLE VII

Fraction No	I V	S F	Palmitic acid %	Palmitic acid Gm	Stearic acid %	Stearic acid Gm	Unsaturated acid %	Unsaturated acid Gm.
S₁	1·0	278·4	67·17	3·557	27·09	1·432	0·074	·003984
S₂	1·01	284·5	46·09	1·100	47·65	1·123	0·074	·001735
S₃	2·25	298·4	..	..	93·64	1·388	1·009	·02434
S₄ (Residue)	4·96	300·7	.		91·62	1·053	3·676	·04225
				4·657		4·976		·07226

Palmitic acid in solid acids	48·37%
Stearic acid in solid acids	51·63%
Palmitic acid in mixed acids	1·76%
Stearic acid in mixed acids	1·88%

The component acids of the oil from the seeds of Solanum nigrum, there-
fore, consist of oleic, linoleic, palmitic and stearic acids. The percentages
are given below in Table VIII.

TABLE VIII

	Wt.%	Mol. %
Oleic acid	49·73	49·57
Linoleic acid	46·63	46·79
Palmitic acid	1·76	1·84
Stearic acid	1·88	1·80

Examination of Unsaponifiable Matter

The unsaponifiable matter extracted from the soap solution with ether was a pale yellow sticky mass, which on crystallisation from absolute alcohol gave a compound m.p. 133° C. the acetyl derivative of which melted at 121–22° C. It gave all colour reactions of a phytosterol. Therefore, it is sitosterol.

The Component Glycerides

The oil was neutralized with sodium carbonate and purified with animal charcoal and Fuller's earth.

One hundred grams of the purified oil was dissolved in six times its weight of dry acetone[11,12] and kept in frigidaire for a week at 0° C. 4·02 grams of solid separated showing the presence of trisaturated or disaturated monounsaturated glycerides or both.

Twenty-five grams of the neutral oil was dissloved in ten times its weight of dry acetone and oxidized[13] with powdered permanganate. The process was repeated twice and in the end nothing remained showing the absence of trisaturated glycerides.

Acetone was distilled off from the filtrate of acetone-chilled oil and the oil, thus left, was dissolved in ten times its weight of dry petroleum ether (40–60° C), cooled to −5° C. and excess of bromine added till the brown colour persisted. It was left in frigidaire overnight. No solid separated. Excess of bromine was destroyed with sodium thiosulphate solution and washed with distilled water, dried over fused calcium chloride and petroleum ether distilled off. The brominated oil was extracted with absolute alcohol and alcohol and acetone (1 : 1) successively. The scheme of separation is given below.

Fractions F_2 and F_3 were debrominated by taking them in methyl alcohol, adding zinc dust (equal in weight to the fraction), passing dry hydrochloric acid gas to saturation and refluxing for eight hours. All the three fractions were then saponified, unsaponifiable matter removed with ether and acids liberated. The saponification values, and thiocyanogen values

Neutral oil (100 gm. (Chilled in acetone)

```
                    |
        _____
        |                                  |
Insoluble F₁ (4·02 gm.)             Soluble   (Filtered and solvent removed,
        |                                      brominated in petroleum ether)
        |                           _____
        |                           |                               |
Insoluble (Nil)                  Soluble   (Washed with   thiosulphate
                                           solvent removed , extracted with
                                           absolute alcohol)
   _____
   |                       |
Insoluble (extracted with alcohol    Soluble   (F₃) 67·76 gm  (dark viscous
        and acetone (1 1)                      liquid)
All dissolved (F₃)
104·8 gm. (brown viscous) liquid
```

of acids were determined   The acids were oxidized with dilute potassium permanganate, extracted with petroleum ether and their saponification values determined.

The results calculated from these values are given in Tables IX, X, XI and XII. These results are in fair agreement with those obtained for the component fatty acids and are given below in Table XI.

TABLE IX

	F₁	F₂	F₃
Wt. of brominated product in gm	..*	67·76	104·8
Wt. of debrominated product in gm	4·02	37·97	57·97
Wt. of unsaponifiable matter in gm	1·0	0 25	0·002
Wt. percent of glyceride (free from unsaponifiable matter)	3·06	38·21	58·73
Sap, Equivalent of liberated acids	279·7	279·1	280·6
Iodine value of liberated acids	32·4	130 2	134·0
Thiocyanogen value of liberated acids	32·14	86·76	89·6
S=p. Equivalent of solid acids	259·2	270·3	280·6
Mol. per cent. of mixed acids	3·06	38·21	58·73

* *N.B.*—Fraction F₁ was got by chilling from acetone and hence was not brominated

TABLE X

Mol   per cent, of acids in each fraction

	F₁ 3·06%	F₂ 38·21%	F₃ 58·73%
Linoleic acid	0·27	48·06	49·19
Oleic acid	33·56	47·93	50·09
Solid acids	66·17	3·91	0·72

Bawa Kartar Singh and Abhay Kumar

TABLE XI

Mol. per cent. of acids on total acids

	F_1 3·06%	F_2 38·21%	F_3 58·73%	Mean 100%
Linoleic acid	0·008	18·36	28·89	47·25 (46·79)
Oleic acid	1·027	18·31	29·42	48·76 (49·57)
Solid acids	2·025	1·54	0·42	3·99 (3·64)

N.B—In fraction F_1 the amount of linoleic acid being too small it may be considered as oleic acid.

The figures in brackets are obtained from component fatty acids (Table VIII)

TABLE XII

Probable component glycerides of the oil of Solanum nigrum (Mol. per cent.)

Glycerides in	F_1 3·06%	F_2 38·21%	F_3 58·73%	Mean 100·0%
1. Fully saturated glycerides	Nil	Nil	Nil	··
2 Disaturated-monounsaturated glycerides	3·06	Nil	Nil	3·06
3 Monosaturated-Diunsaturated glycerides	··	··	··	··
(a) Monosaturated oleolinolein	Nil	4·62	1·26	5·88
4. Triunsaturated glycerides—				
(a) Oleodilinolein	Nil	16·87	27·97	44·84
(b) Dioleolinolein	Nil	16·72	29·50	46·22

N.B.—1. By oxidation of the neutral oil with potassium permanganate in acetone.

2 By chilling the neutral oil in acetone at 0° C

3 & 4 By calculating from the component fatty acids of the brominated glycerides in the oil.

In these calculations the solid acids have been considered as one acid. In view of the fact that the acids distribute themselves evenly in proportion to their amounts, we are justified in assuming that the unsaturated acids in fractions F_2 and F_3 are combined in the glycerides of the *Solanum nigrum* seed oil as monosaturated oleolinolein rather than as monosaturated-diolein and monosaturated-dilinolein. The same may be assumed in case of saturated acids in these fractions as well as in fraction F_1, and as such the probable glyceride structure may be given as follows :—

Dipalmito-olein 2 43%; Palmitostearo-olein 0·63%;

Palmito-oleolinolein 2·48%; Stearo-oleolinolein 3·40%; Oleodilinolein 44·84% and Dioleolinolein 46·22%.

REFERENCES

1. Kirtikar and Basu — *Indian Medicinal Plants*, Vol III, 1748
2. Dey — *Indigenous Drugs of India*, 300
3. Dymock, Warden and Hooper — *Pharmacographic Indica*, Vol. I, 549
4. Pendse — *J. Ind Chem Soc*, 1937, 367–70
5. Saran, B M, and Singh B. K — *Proc Nat Acad Sci (India)*, 1942, **12**, 219
6. Hilditch, T P — *Chemical Constitution of Natural Fats*, 1941 Edition, 371
7. Jamieson and Boughmann — *J Amer. Chem Soc*, 1920, **42**, 1197
8. Dean, H K — *Utilization of Fats*, 72
9. Erbner and Muggenthalor — *Chem Tech & Analysis of Oils, etc*, 5th Edn, Vol I, 568
10. Jamieson and Boughmann — *J Amer Chem Soc*, 1920, **42**, 152
11. Singh, B. K, and Tewari, R. D. — *Proc. Nat Acad. Sci. (India)*, 1943, **13**, 128
12. Hilditch, T P — *Chemical Constitution of Natural Fats*, 1941 Edition, 412–13
13. ————— — *Ibid.*, 405–06

EFFECT OF ADDITION AGENTS ON THE SYNERESIS OF SODIUM OLEATE GELS IN PINENE

By Mata Prasad, G. S. Hattiangdi and S. P. Adarkar

(From the Chemical Laboratories, Royal Institute of Science, Bombay)

The earliest attempt for the quantitative determination of the effect of addition agents on the syneresis of gels was made by Lipatov.[1] He investigated the kinetics of syneresis of geranin gels and observed that the addition of small amounts of sodium chloride and alcohol accelerates the syneretic process, whereas alkali and carbon bisulfide have a retarding effect. Prakash and Dhar[2] observed that the addition of electrolytes increases the velocity of syneresis of a number of inorganic gels. The effect of the addition of a series of alcohols on the syneresis of silicic acid gels has been recently studied by Munro and Monteith[3] who observe that the total volume of the syneretic liquid at equilibrium is the same as that of the control and that no adsorption of alcohol takes place

In a recent communication, Prasad, Hattiangdi and Mathur[4] have mentioned that the addition of certain substances to the solutions of sodium oleate in pinene giving rise to gels, either accelerate or retard their syneretic process. In the present investigation, the effects of a number of addition agents such as soaps, fatty acids, non-aqueous solvents and other organic substances on the syneretic phenomenon exhibited by sodium oleate gels in pinene have been exhaustively studied. A few of these results have been communicated by Hattiangdi[5] in connection with the stability of soap gels in non-aqueous media, but no attempt has been made therein to explain the behaviour of the various addition agents on the phenomenon of syneresis

EXPERIMENTAL TECHNIQUE

The sodium stearate used was a Merck's product, whereas sodium oleate, sodium palmitate and potassium stearate were pure products of the B. D. House. The pinene used in the preparation of gels was obtained from Messrs. Eastman Kodak and Co., and was the fraction distilling at 156°. Benzene, toluene, xylene, mesitylene, aniline, phenylene-diamine, oleic acid, stearic acid and palmitic acid were Merck's pure products; the nujol used was a product of Stanco Inc. Co.

320

The gel-forming solutions of sodium oleate in pinene were prepared in test-tubes of the same diameter ($2r = 1.45$ cm.) as described by Prasad and Hattiangdi[6] and small known amounts of different substances were added; the hot homogeneous solutions were then allowed to cool, gelate and synerise in a water thermostat maintained at 30° C. The amount of synereticum exuded after a fixed time interval was determined by the method employed by Prasad and co-workers.[4] The results presented in all the tables in this paper are represented on a percentage basis, the amount of synereticum exuded by sodium oleate gel in pinene without any addition agent being taken as a standard for comparison of the degrees of accelera-tion or retardation.

DISCUSSION OF RESULTS

Effects of the Addition of Alkali Soaps.—Experiments on the addition of sodium stearate, sodium palmitate and potassium stearate on the synere-tic process were performed on the system consisting of 0·09 g. of sodium oleate in 10 c.c. of pinene The results show that all these three soaps retard the syneretic process. On plotting the amounts of synereticum exuded at any fixed time interval against the amounts of the soap present in the system, regular smooth curves are obtained which fall rapidly in the beginning and then gradually as the soap content is increased, and finally intersect the concentration axis at some point. The nature of these curves shows that as the concentration of the added soap is gradually increased, the retarda-tion is rapid in the beginning and slows down continuously till a stage is reached at some optimum concentration when the syneretic process is com-pletely stopped. The retarding effects of the three soaps at an interval of one hour from the commencement of experiments are given in Table 1.

TABLE I

Amount of soap added (in g.)	Percentage Retardation		
	Sodium stearate	Sodium palmitate	Potassium stearate
0·005	..	62·1	..
0·007	..	70·9	..
0·010	27·9	78·7	70·1
0·015	..	90·0	..
0·020	51·0	..	79·0
0·030	62·7	..	..
0·040	..	..	86·2
0·050	87·5	..	89·1

It will be seen from the results given above that all the soaps retard and finally tend to stop the syneresis of sodium oleate gels in pinene, the retarding effect
A2a

being in the order of NaP > KSt > NaSt. It was observed qualitatively that gels of sodium stearate, sodium palmitate and potassium stearate in pinene synerise to a very slight extent and the apparent order is NaP < KSt < NaSt. The parallelism between the retarding effects of the soaps and the synerising capacity of their gels in pinene explains the retarding effect on the syneretic process of sodium oleate gels in pinene when small amounts of either of these soaps are present in the synerising system.

Effect of the Addition of Fatty Acids.—The effects of the addition of oleic, stearic and palmitic acids on the syneretic phenomenon exhibited by sodium oleate gels in pinene were investigated on a system consisting of 0·09 g. of the soap dissolved in 10 c.c. of pinene. The results obtained are presented Table II.

TABLE II

Amount of acid added (in g.)	Percentage Retardation		
	Oleic acid	Stearic acid	Palmitic acid
0·01	System does not set to a gel	System does not set to a gel	8·5
0·02			22·6
0·03			77·5
0·04			93·3
0·05			95·7
0·10	Non syneretic gel is obtained		System does not set to a gel

It is interesting to note that the effects of the three closely related fatty acids on the syneretic phenomenon are totally different from one another. Oleic acid when present even in very small quantities prevents the gel-forming system from setting to a gel; the system is transparent when hot but develops considerable opacity on cooling. If the oleic acid content is slowly increased, it is found that in the neighbourhood of 0·1 g., the system sets to a firm transparent gel. This gel does not synerise and neither does it develop opacity when kept for a sufficiently long time. This behaviour of oleic acid is unique.

In the presence of stearic acid, it is found that the system does not set to a gel even when the acid content is varied over a sufficiently large range. A gel is obtained when small amounts of palmitic acid are present in the system and the syneretic process is retarded, the extent of retardation increasing as the acid content is increased from 0·01 g. to 0·05 g. When the acid content is increased slightly beyond 0·05 g., the system yields a loose viscous mass instead of giving a rigid, transparent gel.

It would be interesting to mention here that Miss Laing[7] studied intensively the state of oleic acid and potassium oleate in solution in dry alcohol, and concluded that a small amount of a complex compound is formed in this system, which is responsible for the slight yet distinct tendency of all such solutions towards opalescence and frothing. The development of opacity by mixtures of sodium oleate and the various acids in pinene when they are cooled can probably be explained in the same manner.

Effect of the Addition of Non-Aqueous Media —The results of the experiments on the effects of the addition of a number of non-aqueous media on the syneretic phenomenon exhibited by sodium oleate gels in pinene are given in Tabels III, IV and V. The synerising system investigated in all these cases consisted of 0·09 g. of sodium oleate dissolved in 7 c.c. of pinene. The various results have been presented in three different tables for the sake of convenience during discussion.

TABLE III

Non-aqueous media added (in c c.)	Percentage Acceleration or Retardation			
	Benzene (Retardation)	Toluene (Retardation)	Xylene (Acceleration)	Mesitylene (Acceleration)
0·1	2·6	..	11·5	..
0·2	..	12·8	..	..
0·3	13·0	..	16·2	..
0·4	..	11·5	..	..
0·5	20·8	13·2	14·2	17·2
0·6	..	16·1	..	..
0·8	..	12·8	..	..
1·0	25·9	9·4	10·8	27·6
2·0	22·4	9·3	6·1	19·9
3·0	22·4	9·4	5·8	17·8

It will be seen from the above table that although small amounts of benzene or toluene retard the syneretic process, yet the effect is not great in as much as synerisis is not stopped. On increasing the amounts of any one of these substances, the percentage retardation first increases and then decreases to a constant value. Xylene and mesitylene, even when present in small quantities, accelerate the syneretic process of the system and in this respect behave differently from benzene and toluene. The acceleration which is noticed in the presence of small amounts of xylene or mesitylene is not largely affected by the addition of larger amounts of these substances.

It has been qualitatively observed that sodium oleate gels in benzene and toluene synerise but the extent of synerisis is not so pronounced as in the case of pinene; the addition of increasing amounts of either benzene

A3

or toluene would, therefore, tend to exert a slightly retarding effect on the syneresis of the system, but the actual process of exudation of liquid is not stopped altogether. The gels of sodium oleate in xylene and mesitylene have been observed to synerise more profusely than those in pinene, and hence on the basis of the aforesaid considerations, the syneresis of the sodium oleate gels in pinene is slightly accelerated by the addition of small amounts of either of these substances

An interesting observation can be made from the data presented in Table III, that whereas there is retardation of the syneretic process in the presence of benzene, the percentage retardation decreases on the addition of the same amount of toluene, and xylene and mesitylene actually accelerate the syneretic process. Thus, the addition of benzene, toluene, xylene

Fig 1
—CH₃ group
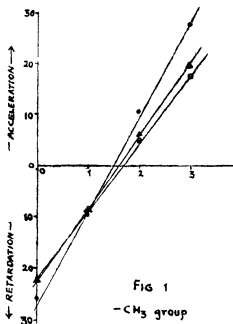
and mesitylene which differ from each other in the increasing number of —CH₃ groups modifies the syneretic process of sodium oleate gels in pinene in a definite manner In order to determine the relationship between the percentage retardation or acceleration for the same amounts of benzene, toluene, xylene and mesitylene and the number of —CH₃ groups contained in these substances, the values of the two have been plotted and the curves obtained are shown in Fig. 1 In all cases, these curves are straight lines which shows the existence of a linear relationship between the two factors.

The effect of the addition of aniline and phenylene diamine on the syneretic phenomenon exhibited by sodium oleate gels in pinene is given in Table IV.

TABLE IV

Amount of substance added (in g.)	Percentage Acceleration or Retardation		
	Benzene (Retardation)	Aniline (Acceleration)	Phenylene diamine (Acceleration)
0·0924	10·3	17·1	167·1
0·0600	19·0	25·0	186·7
0·1468	22·6	32·5	112·5
0·2368	25·0	38·1	94·7

It will be seen from the above table that whereas benzene retards the syneretic process slightly, aniline and phenylene diamine accelerate it, the latter having a greater accelerating power than aniline. In this respect, their behaviour is analogous to that of xylene and mesitylene.
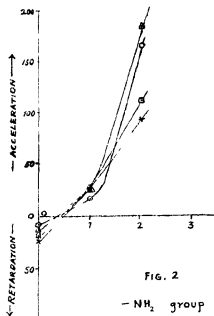
FIG. 2

$-NH_2$ group

An attempt was made to see if any relationship exists between the percentage retardation or acceleration and the number of $-NH_2$ groups. The plot of the values of the two factors is shown in Fig. 2 It is apparent that in no case is the linear relation obtained. This behaviour is to be expected

because whereas the retardation in the case of benzene and the acceleration in the case of aniline proceed regularly, that is slowly increase, the acceleration in the presence of phenylene diamine proceeds in the reverse manner, that is it goes on decreasing instead of increasing from the very beginning.

Attempts were then made to establish definitely the truth of these empirical relationships by employing compounds containing different number of −OH groups. It was found that among the aromatic compounds containing −OH groups only phenol is miscible in pinene whereas other substances (resorcinol, pyrogallol and phloroglucinol) charred on slight warming with the gel-forming solution. The aliphatic compounds, namely the alcohols, were miscible in pinene in all proportions, but even very small amounts of either of the alcohols were observed to increase the solubility of the soap to such a great extent that it remained in solution and did not set to a gel even after keeping for a very long time.

The data regarding the effect of the addition of nujol on the synerising system of sodium oleate in pinene is given in Table V.

TABLE V

Amount of nujol added (in g.)	Percentage Retardation
1·0	45·7
2·0	82·2
2·5	89·2
2·7	91·5
2·9	93·2
3·0	94·4
3·5	96·2
4·0	97·6

It is evident that small amounts of nujol considerably retard syneresis and if the nujol content is slowly increased the retardation goes on increasing till a stage is reached when syneresis is completely stopped. In this respect the retarding effect of nujol can be compared to that of either of the soaps discussed earlier. The behaviour of nujol may possibly be explained on the basis that gels of sodium oleate in this medium are quite firm and synerise to a very slight extent Hence, with increasing amounts of nujol present in the system, the syneretic process is considerably retarded in the earlier stages and tends to stop completely in the presence of higher nujol content.

Prasad and co-workers[4] have explained the syneretic phenomenon exhibited by sodium oleate gels in pinene on the consideration that (i) the colloidal particles in the gel-forming solution are bound to each other by

residual valencies more loosely than in a crystal, and (ii) when the arrangement of the structural units is unstable, that is, the forces of residual valencies are weak, the gel shrinks due to progressive association and probably due to the orientation of the structural units, ultimately resulting in the exudation of interstitial liquid. On this hypothesis, the observed effects (acceleration and retardation) of the various addition agents on the syneretic process can be explained as follows.

The presence of small amounts of certain addition agents (soaps, acids, etc.) in the gel-forming system of sodium oleate in pinene favours the formation of complex compounds which brings about changes in the internal packing, depending upon the constitutive nature of the added substance. The addition agents also considerably influence the binding forces and consequently the shrinkage of the gel due to association of the structural units which depends upon these forces and the consequent exudation of the liquid is also correspondingly modified. If the binding forces are increased due to the addition of certain substances (soaps, acids, etc.) the system becomes more stable and is less susceptible to shrinkage and therefore retards the syneretic process. Addition of other substances such as xylene, mesitylene, etc., apparently tends to weaken the forces of attraction between the micelles and hence the structure becomes more unstable and shrinks more spontaneously exuding a considerably large amount of the interstitial liquid in this process.

SUMMARY

The effect of a number of addition agents on the syneretic phenomenon exhibited by gels of sodium oleate in pinene has been investigated. The addition agents employed are sodium stearate, sodium palmitate, potassium stearate, oleic acid, stearic acid, palmitic acid, benzene, toluene, xylene, mesitylene, aniline, phenylene diamine and nujol

The soaps retard and tend to stop the syneretic phenomenon, the retarding effect being in the order of NaP > KSt > NaSt The effects of the three closely related fatty acids on the syneretic phenomenon are totally different from one another Benzene and toluene retard the syneretic process but xylene and mesitylene accelerate it. There appears to exist an approximately linear relationship between the percentage retardation or acceleration for the same amount of benzene, toluene, xylene and mesitylene, and the number of $-CH_3$ groups contained in these substances. No such relationship can be observed in the case of amino compounds among which benzene retards and aniline and phenylene diamine accelerate the syneretic process.

A4

The retarding effect of nujol, a heavy paraffin oil, on the syneretic
process is analogous to that of either of the soaps used in this investigation
inasmuch as syneresis is retarded and there is a tendency to stop it altogether.

An attempt has been made to explain the various behaviour on theo-
retical considerations.

REFERENCES

1 Lipatov   *Koll Z , 1929, 49, 441 , J Russ. Phys*
                        Chem Soc., 1930, 62, 39.
2 Prakash and Dhar   *J Indian Chem Soc., 1930, 7, 417*
3 Munro and Monteith . *Can J Research, 1942, 20 (B), 212*
4. Prasad, Hattiangdi and *Proc Ind. Acad. Sci , 1945, 21, 105.*
   Mathur
5. Hattiangdi   Communicated for publication.
6 Prasad and Hattiangdi *Proc. Ind. Acad Sci , 1945, 21, 1*
7. Miss Laing   *J C. S., 1918, 113, 435*

RAMAN SPECTRA OF THE SECOND ORDER IN CRYSTALS

Part III. Quartz

By R. S. KRISHNAN

(From the Department of Physics, Indian Institute of Science, Bangalore)

1 REVIEW OF THE PREVIOUS WORK

As clear pieces of quartz are readily available, it is one of the most frequently examined crystals in Raman effect studies The earliest investigations were those of Landsberg and Mandelstam (1928) at Moscow and of K. S. Krishnan (1928, 1929) at Calcutta. Subsequent studies of the Raman effect in quartz were carried out in many laboratories, notably by Rao (1928), Daure (1929) and Nisi (1929). The last two authors recorded the maximum number of Raman lines, namely ten. A little later, Gross and Romanova (1929) made a comparative study of the Raman and infra-red absorption spectra of crystalline and amorphous quartz. With the λ 4358 radiation of the mercury arc and exposures of the order of 120 hours, they succeeded in recording 19 Raman lines, including 7 very faint ones, and catalogued the frequency shifts and their estimated relative intensities Using the λ 2536 5 mercury resonance radiation as exciter and giving an exposure of only 20 minutes, Rasetti (1932) recorded a spectrum which exhibited 14 lines with frequency shifts 128 6, 207·3, 265·9, 356·5, 394 4, 403·9, 466·4, 696·8, 796·9, 809·3, 1063 1, 1082·5, 1160·2 and 1227 1 cm⁻¹ He was the first to establish the doublet structure of the Raman lines at about 400, 800 and 1075 cm⁻¹ Kujumzelis (1935, 1936) carried out a detailed and comparative study of the Raman spectra of fused and crystalline quartz and of different optical glasses Besides confirming the results obtained by Rasetti for crystalline quartz, Kujumzelis reported the existence of some fainter lines with frequency shifts 530, 570–600, 740, 860–950, 1100 and 1400–1600 cm⁻¹ Nedungadi (1940) and Saksena (1940) independently carried out a careful and detailed investigation of the Raman spectrum of crystalline quartz using the 4046 and 4358 radiations of the mercury arc as exciter. These authors were unable to record the feebler lines reported by Gross and Romanova and by Kujumzelis. Using the Rasetti technique and giving long exposures, Roop Kishore (1942), however, succeeded in observing a set of feeble Raman lines in the region 860–950 cm.⁻¹

329

The effect of temperature on the intensity of the Raman line at 466 cm.$^{-1}$ in crystalline quartz has been studied by several workers, viz., Landsberg and Leontowitsch (1929), Brickwedde and Peters (1929), Landsberg and Mandelstam (1929, 1930), Ornstein and Went (1935), and Venkateswarlu (1941). They showed that the ratio of the intensities of the Stokes and the anti-Stokes lines was in accordance with the modified Boltzmann formula. Sharp disagreements with the existing theories have been reported as regards the individual intensities of the Stokes and anti-Stokes lines. The influence of temperature on the frequency shift and width of the Raman lines in quartz has been studied by Ney (1931) over the range of temperature from 18° to 500° C. and by Nedungadi (1940) over the range from − 180° C. to 530° C. Nedungadi drew attention to the extraordinary behaviour of the line 207 cm.$^{-1}$ It broadens enormously at higher temperatures and in an unsymmetrical manner with respect to its original position and ultimately disappears into a continuum as the transition temperature (575° C.) is approached. Raman and Nedungadi (1940) suggested that the remarkable behaviour of the line 207 with rise of temperature has a special significance for the α–β transformation of quartz which takes place at 575° C.

Cabannes (1929), Menzies (1929), Bouhet (1937), Cabannes and Bouhet (1937), Michalke (1938) and Saksena (1940) investigated the effect of crystal orientation on the intensity and polarisation of the Raman lines in quartz. On the basis of the results obtained from such studies, they have attempted to classify the frequency shifts of the Raman lines. Cabannes, Menzies and Michalke used incident unpolarised light, whereas Cabannes and Bouhet worked with incident circularly polarised light. Saksena who made a thorough investigation of the problem used incident light polarised in different azimuths. He has given a more or less correct and complete classification of the principal lines observed in the spectrum of quartz and also identified the corresponding fundamental modes of internal vibration of the atoms in the unit cell. The results obtained by Saksena will be referred to in detail later in this paper.

Some miscellaneous investigations have also been reported in the literature concerning the Raman effect in quartz. Weiler (1932) examined the Raman spectra of a series of silicic acid esters and gels and compared the characteristic frequencies of the SiO_2 group in these compounds with those of crystalline and fused quartz. Ornstein and Went (1935) investigated the dependence of the intensity of the Raman lines of quartz on the wave-length of the exciting line. The λ^{-4} law was found to be obeyed.

It is evident from what has been said above that neither Rasetti (1932) nor Roop Kishore (1942) fully utilised the power of the Rasetti technique. By using

the λ 2536·5 mercury radiation as exciter and giving exposures of the order of 48 hours for a crystal 15 cm. long, the author (Krishnan, 1945) recorded a very intense spectrum of quartz in which 41 distinct frequency shifts were observed and measured. In the preliminary report which appeared in *Nature*, provisional assignments were given for most of the lines Since then the subject has been further investigated by the author and more complete results are presented in this paper.

2. DETAILS OF THE EXPERIMENT

A few transparent and practically colourless specimens of quartz with well developed faces were selected for the present study from Sir C V. Raman's personal collection. The biggest one was about 7" long and 2½" thick. One end of each specimen was cut normal to the optic axis. This end face was then ground and polished. The construction of the mercury arc and the optical arrangement used for investigations on the Raman spectra of crystals have already been described in Part I (Krishnan, 1945) of this series

The crystal to be examined was mounted with its optic axis vertical and with one of its long hexagonal sides facing the most intense portion of the arc. The light scattered along the optic axis was focussed on to the slit of a quartz spectrograph with the aid of an aluminised mirror and a condensing lens.

As in the case of calcite and gypsum, two quartz spectrographs (Hilger E1 and E3) were used for recording the Raman spectrum. The higher dispersion instrument was employed in order to measure the frequency shifts and widths of the principal Raman lines very accurately. For this purpose, an iron arc comparison spectrum was photographed at the centre of the Raman spectrum. With a slit-width of 0·03 mm. and using a crystal 2" long, exposures of the order of three days were given to get a satisfactory spectrum with the high dispersion instrument.

The E3 spectrograph was employed for recording an intense spectrum of quartz showing as many second order Raman lines as possible. For this purpose, the biggest crystal was used. With a slit-width of 0 03 mm, exposures of the order of three to four days were given to obtain intense photographs.

All the negatives were measured under a Hilger cross-slide micrometer.

3. RESULTS

First Order Spectrum.—The spectrogram taken with the high dispersion instrument showing the first order spectrum of quartz is reproduced in Fig. 1. The microphotometer record of the same is reproduced in Fig. 2,

The spectrum consists in the main of 12 first order or principal Raman lines including two doublets   The frequency shifts together with relative intensities of the lines are given in Table I.   The values reported earlier by Rasetti (1932) and Saksena (1940) are also included for purposes of comparison. The author's results agree closely with those of Rasetti except for the doublet at about 800 cm.⁻¹   The intensity and width of the pair of lines at about 800 cm.⁻¹ are found to be markedly influenced by crystal orientation (Saksena, 1940).   It is quite probable that the orientation of the crystal in Rasetti's experiment was different from the one adopted in the present investigation.

TABLE I

Frequency Shifts of the First Order Raman Spectrum of Quartz

No	Rasetti	Saksena	Author	Class
1	128	128	127·7 (20)*	E_1
2	207·3	207	206·4 (15)	A_1
3	265·9	267	266·1 (8)	E_2
4	356·5	358	357·2 (7)	A_2
5	{ 394·4	391	394 8 (7)	E_3
	{ 403·9	403	403 8 (6)	
6	466 4	466	466·0 (30)	A_3
7	696·8	695	696·4 (5)	E_4
8	{ 796·9	795	794·7 (6)	E_5
	{ 809·3	806	808 8 (6)	
9	1063·1	1063	1063·7 (5)	E_6
10	1082·5	1082	1081·9 (4)	A_4
11	1160·2	1160	1159·3 (8)	E_7
12	1227	1228	1228 0 (4)	E_8

* The figures enclosed in brackets represent the relative intensities of the lines on an arbitrary scale   They were estimated from the micro-photometric record of the spectrogram (reproduced in Fig. 3) which was taken with the optic axis of the crystal perpendicular to the incident and parallel to the scattered rays, the illuminating beam being unpolarised.

Second Order Spectrum.—A heavily exposed photograph of the Raman spectrum of quartz taken with the E3 spectrograph is reproduced in Fig. 3 together with a photograph of the direct arc.   The microphotometric records of the same are shown in Fig. 4.   The second order Raman lines can be clearly seen in the microphotometric record.   Most of them can also be identified in the reproduced photograph.   In addition to the first order Raman lines already listed in Table I, the spectrum of quartz as recorded here consists of 29 Raman lines, some of which have intensities comparable with those of the first order lines.   The positions as well as the frequency shifts of most of them have been marked in Fig. 4   Some of the lines fall very close to the very intense principal Raman lines and as such, they are not seen resolved either in the photograph reproduced in Fig. 3, or in its

microphotometric record reproduced in Fig. 4. Such lines are, however, clearly discernible in the photograph taken with the high dispersion instrument. Their positions are indicated in Figs. 1 and 2.

The frequency shifts of the more intense second order Raman lines were evaluated from measurements made on the negatives, whereas those of the feebler ones were estimated from the microphotometric records. In order to be sure of the existence of each and every second order line reported here, microphotometric records not only of different spectrograms, but also of different regions in the same spectrogram were taken and compared. Care was taken to eliminate those Raman lines which could reasonably be assigned as first order Raman shifts excited by other mercury lines.

The 29 second order Raman lines have been classified into two groups and their frequency shifts have been listed separately in Tables II and III.

TABLE II

Second Order Raman Lines explicable as Octaves and Combinations of the Fundamentals listed in Table I

No	Frequency Shifts in cm^{-1}	Assignment	Calculated Frequency Shifts
1	488	$A_2 + E_1$	485
2	530	$2E_2$, $E_1 + E_3$	532, 527
3	730	$A_2 + E_2$	732
4	864	$A_3 + E_3$	868
5	890	$B_2 + E_3$	888
6	925	$E_1 + E_3'$	928
7	961	$E_2 + E_4'$	962
8	980	$2B_3$	976
9	1260	$A_1 + E_6$; $A_3 + E_5$	1269, 1266
10	1290	$A_1 + A_4$	1288
11	1394	$2E_4$	1393
12	1444	$A_2 + A_4$	1439
13	1495	$E_3 + E_5$	1494
14	1630	$E_3 + E_6$, $A_3 + E_7$	1628, 1625
15	2126	$2E_6$	2126
16	2240	$A_4 + E_7$	2241
17	2420	$B_4 + E_8$	2418

TABLE III

Raman Lines not explicable as Octaves and Combinations of the Fundamentals Listed in Table I (Super-Lattice Lines)

No.	1	2	3	4	5	6	7	8	9	10	11	12
Frequency shifts	39	95	145	170	240	452	509	548	588	842	944	1040
Relative intensity	1	2	3	2	2	7	4	2	0	1	0	0

The lines with frequency shifts 509, 530, 588, 730 and 944 cm.$^{-1}$ have already been reported by Gross and Romanova (1929). The existence of the line at 452 cm.$^{-1}$ (see Table III) was first reported by Cabannes and Bouhet (1937), and later confirmed by Nedungadi (1940). Saksena showed that by suitably polarising the incident light, the 466 line could be greatly weakened and the two companions at 452 and 488 cm $^{-1}$ could then be clearly observed The two lines with frequency shifts 95 and 145 cm.$^{-1}$ came next in the order of intensities (see Table III) The existence of these two low frequency shifts was first pointed out by Norris (1941) after a careful scrutiny of the spectrograms taken by Nedungadi and Saksena, and his findings have been confirmed. The remaining lines listed in Tables II and III have been recorded for the first time.

4   DISCUSSION OF RESULTS

α-Quartz belongs to the trigonal subdivision of the hexagonal system, the symmetry class being trigonal enantiomorphous hemihedral. The space group is represented by $D_3{}^4$. The unit cell contains three molecules of SiO_2. Each silicon atom is surrounded by four oxygen atoms, and each oxygen atom has two silicon atoms as near neighbours. The four oxygen atoms round a silicon atom do not form a regular tetrahedron.

Principal Frequencies of Quartz.—On the basis of the above structure and on the assumption that the repeating unit in the dynamic crystal is the simple unit cell. Went (1935) discussed the $(3p - 3)$ so-called fundamental modes of oscillation of the quartz lattice. Since p, the number of non-equivalent atoms in the unit cell, is 9 for quartz, the number of modes is 24. Owing to the degeneracy of some of the modes of oscillation, the number of distinct frequencies is reduced to 16, distributed as follows :— 4 coming under the A class active only in Raman effect, 4 of the B class active only in infra-red absorption, and 8 of the E class active in both. But Went's assignments of the observed frequencies were not correct as they were based on the insufficient polarisation data presented by the earlier workers.

A complete group-theoretical analysis of the normal modes of internal oscillation of the quartz lattice has been worked by Saksena (1940, 1942) According to his analysis the group of 3 silicon and 6 oxygen atoms present in the unit hexagonal cell has 16 principal modes of vibration with distinct frequencies. The assignments of the observed principal Raman frequencies are shown in column 5 of Table IV. They have been made on the basis of their relatively large intensities and also on the polarisation data given by Saksena. These assignments are in agreement with those of Saksena except as indicated in the following paragraphs.

TABLE IV

Class	m	Raman	Infra-red	Observed frequencies in cm.$^{-1}$
A	4	p	f	206·4 ; 357·2 ; 466·0 , 1081·9
B	4	f	p	385 ; 488 ; 800 ; 1111–1190
F	8	p	p	127·7, 266·1 ; 394·8–403·8 ; 696·4 ; 794·7–805·8
				1063·7 ; 1159·3 ; 1228·0

The notations have the usual significance as understood in group theoretical analysis.

The four principal frequencies coming under class B (see Table IV) have been assumed from the infra-red measurements of Plyler (1929) as $B_1 = 385$, $B_2 = 488$, $B_3 = 800$ and $B_4 = 1111$–1190 cm.$^{-1}$ Saksena took them as 364, 508, 777 and 1149 cm.$^{-1}$ on the basis of the observed positions of infra-red reflection maxima.

The line 1228·0 cm.$^{-1}$ has been taken by the author as one of the principal frequencies coming under the E class for the reason that it appears with very high intensity for some orientations of the crystal and that it is one of the twelve principal frequencies recorded by Rasetti. Moreover, the frequency shift of this line cannot be reasonably accounted for as an octave or a combination of the other principal frequencies listed in Table I. Saksena, on the other hand, has taken a line at 479 cm.$^{-1}$ as one of the E class fundamentals in place of the line 1228 cm.$^{-1}$ and is inclined to treat the latter as a combination Raman line on the following scheme :

$$B_3 \ (777) \ + 2A_3 (466) - E (479) \sim 1228.$$

Thus, according to Saksena's assignment, the 1228 line is a quarternary combination. Apart from the fact that such an assignment is far fetched, if we take the correct value of B_3, namely 800 cm.$^{-1}$ and not 777 cm.$^{-1}$ as taken by Saksena, the calculated frequency shift would be in excess of the observed value by 25 wave numbers.

In the infra-red absorption spectrum, the high frequency oscillation appears as a doublet with frequency shifts 1111 and 1190 cm.$^{-1}$ It is probably correct to take the fundamental as 1150 cm.$^{-1}$ which has suffered a Fermi splitting on account of the fact that the combination B_1 (385) + B_3 (800) and the infra-red active E_7 (1159) fall in the region of the doublet. Analogous explanation has already been offered by Saksena for the appearance of the pairs of lines at 394·8, 403·8 cm.$^{-1}$ and 794·7, 805·8 cm.$^{-1}$ in the Raman effect.

Combinations of the Principal Frequencies.—Applying the ordinary selection rules, it can be shown that in the second order Raman spectrum,

besides the overtones of the principal frequencies, the following combinations, namely $A_l + E_m$, $B_l + E_m$, $A_l + A_m$, $B_l + B_m$ and $E_l + E_m$ are allowed to appear. The subscripts l and m can take the values 1 to 4 in the case of A and B and 1 to 8 in the case of E. On this basis, satisfactory assignments have been given to the 17 Raman lines appearing in the second order spectrum of quartz and listed in Table II. The assignments as well as the calculated frequency shifts are included in the same table.

The overtones of the four infra-red active B class frequencies should be expected to appear in Raman effect with appreciable intensity. In the recorded spectrum, the overtone of 488 cm.$^{-1}$ appears as a separate line with frequency shift 980 cm.$^{-1}$ The appearance of the octave of 385 cm.$^{-1}$ is indicated by the presence of a point of inflexion on the slope of the intense doublet at about 800 cm.$^{-1}$ (see Fig. 4). Two additional lines with frequency shifts 1596 cm.$^{-1}$ and 2225 cm.$^{-1}$ have been marked in Fig. 4, although they are not listed in Table II. The former one can be assigned as the octave of B_3 (800 cm.$^{-1}$) and/or as an anti-Stokes Raman shift 128 cm.$^{-1}$ excited by λ 2652·0, while the latter can be assigned as the first order Raman shift 466 cm.$^{-1}$ excited by λ 2655·1 and/or the octave of the infra-red frequency B_4 (1111 cm.$^{-1}$). The octave of 1190 cm^{-1} even if present, would not be detected as it would fall roughly on the mercury line λ 2698·9.

Besides the 29 Raman lines already accounted for, there are no fewer than 12 Raman lines the frequency shifts of which are listed in Table III. The intensities of some of them are comparable to those of the less intense principal lines. Attempts have been made to explain these lines as combinations. None of them could be reasonably assigned as a summational since the values of the observed frequency shifts do not correspond to the sums of the principal frequencies taken two by two. A differential can appear in the Raman effect only if the corresponding summational is allowed (viz., Herzberg, 1945). The intensity ratio of the differential to the corresponding summational is roughly given by the Boltzmann factor. Herzberg has drawn attention to the important result that the wave number of a differential should be exactly equal to the difference of the wave numbers of the constituent Raman lines even if anharmonicity is taken into account, whereas the wave number of a summation line is not exactly the sum of the wave numbers of the individual lines. In the light of the above principles, it is impossible to explain any of the frequency shifts of the Raman lines listed in Table III as differentials of the 16 principal frequencies of internal oscillation of the quartz lattice.

Super-Lattice Frequencies.—The fact thus emerges that a whole series of frequency shifts in the Raman spectrum of quartz are incapable of being

assigned either as one of the $(3p - 3)$ so-called fundamental modes of oscillation of the lattice or as octaves or combinations thereof. The appearance of these Raman lines which cannot be understood on the basis of the usual theories of crystal dynamics, however, finds an explanation in the new theory of crystal dynamics put forward by Sir C. V. Raman (1943). According to this theory, every crystal has not $(3p - 3)$ but $(24 p - 3)$ fundamental modes of atomic vibration with monochromatic frequencies. Of this number, $21p$ modes are oscillations of the lattice in which the equivalent atoms in adjacent cells along 1, 2 or 3 crystallographic axes vibrate in opposite phases. In the case of quartz, $p = 9$ and hence, there should be 189 such modes of super-lattice oscillations. The actual number of distinct frequencies would be considerably less because of the symmetry of the crystal and consequent degeneracy of some of the modes of oscillation In the super-lattice oscillations, the equivalent atoms in the adjacent cells vibrate in opposite phases and the variations of optical polarisability produced in different cells therefore cancel out to a first approximation Consequently, the super-lattice oscillations would be inactive as fundamentals in the Raman effect They can, however, manifest themselves as octaves and as allowed combinations in the second order Raman spectrum. But a great majority of them would be extremely weak because of the very nature of these oscillations. It is not surprising therefore, that the recorded spectrum exhibits only a very limited number of super-lattice lines In this connection, it is noteworthy that out of the 12 lines observed, the lines with frequency shifts 95, 145, 170, 240, 452, 509 and 842 cm.$^{-1}$ appear in the vicinity of some of the extremely intense principal frequency shifts, *viz.*, 128, 206, 466 and 800 cm.^{1} and it appears not at all unlikely that the former have borrowed intensity from the latter by a kind of *Fermi resonance*

5. Thermal Energy of Quartz

On the assumption that quartz has only sixteen fundamental vibration frequencies as suggested by Saksena, the specific heat of quartz between $25 \cdot 8°$ T. and $808 \cdot 6°$ T has been recalculated, taking the values of the frequency shifts as those given in Table IV The second column in Table V gives the sum-total of the contributions of the 24 Einstein terms Column 3 gives the Debye correction term for the remaining three degrees of freedom. The limiting frequency for the Debye function is assumed to be that obtained by Norris (1941) from the data on elastic constants of quartz. Column 4 gives the calculated value of the total C_v. The observed values of C_v at various temperatures were taken from Norris' paper and shown in column 5 of Table V It is seen from the table that there is no satisfactory agreement between the observed and the calculated values of the specific heat throughout

the range of temperature investigated. This suggests that the fundamental assumption on which the calculation of the specific heat is based is wrong; the fundamental modes of vibration of the quartz lattice are not $(3p - 3)$, i.e., 24, but $(24p - 3)$, i e., 213 in number Before a proper evaluation of the specific heat could be made, it is necessary to know the frequencies of the various possible modes of super-lattice oscillation and their respective degeneracies.

TABLE V

Temperature	Einstein Term Contribution $\sum_i RE\left(\frac{h\nu_i}{kT}\right)$	Debye Term Contribution according to Norris	Total Cv Calculated	Total Cv Observed	Deviation
T°					
25·8	0·17	0·39	0·56	1·25	·69
28·75	0·29	0·53	0·82	1·56	·74
38·1	0·70	0·96	1·66	2·38	·72
53·4	2·03	2 14	4·17	4·65	·48
60·3	2·67	2·57	5·24	5·56	·32
80·0	4·55	3·57	8·12	8·58	·46
98·9	6·47	4·20	10·67	11·04	·37
122·1	8·82	4·72	13·54	14·29	·75
156·2	12·10	5 14	17·24	18·69	1·45
184·8	14·63	5·36	19·99	21·99	2·00
216·1	17·28	5·52	22·80	25·07	2·27
252·1	20·11	5·62	25·73	28·34	2·61
272·0	21·63	5 68	27·31	30·34	3·03
298·1	23·31	5·71	29·02	31·49	2·47
381·1	28·67	5·81	34·38	36·84	2·46
428·8	30·96	5·84	36·80	39·16	2·36
475·8	33·04	5·86	38·90	41·25	2·35
565·3	36·25	5·88	42·13	44·54	2·41
670·0	38·99	5·91	44·90	46·82	1·92
777·3	40·71	5·92	46·63	48·68	2·05
808·6	41·16	5·92	47 08	49·09	2·01

6 BRILLOUIN COMPONENTS

A comparative study of the photographs and microphotometric records reproduced in Figs. 3 and 4 shows that the width of the exciting line λ 2536·5 and its intensity relative to that of its neighbour λ 2534·8 are enhanced in the spectrum of the scattered light from quartz. The increase has to be attributed to the presence of Brillouin components which are not absorbed by the column of mercury vapour Although they have a finite wave number separation from the unmodified line, they are not seen separated from the latter because of the low resolving power of the spectrograph used. Similar observations have already been reported by the author in the case of calcite and gypsum. Quartz, however, shows the phenomenon most prominently It was therefore thought desirable to examine the so-called unmodified scattered radiation in quartz with the aid of a high resolving power interferometer, namely, a Fabry-Perot etalon. Unlike the λ 4680,

4722 and 4810 zinc arc lines, the λ 2536·5 mercury resonance radiation has five equally intense hyperfine structure components close to one another which give the line a width of about 0·75 cm.⁻¹ This fact precludes the mercury resonance radiation being used for quantitative studies of the Doppler effect in light-scattering in crystals.

Using the Rasetti technique and an aluminised Fabry-Perot etalon (1 mm. separation), the author has successfully photographed the Brillouin components in quartz. Photographs (a) and (e) in Fig. 5 show the interference pattern of the 2536·5 radiation taken through the intermediate spectrograph. Photographs (b). (c) and (d) show the patterns of the same radiation after scattering in a crystal of quartz. The Brillouin components* can be clearly seen in the photographs. The first is for the case of backward scattering along the optic axis, the second for backward scattering perpendicular to the optic axis, and the third one for the case of transverse scattering, the illumination being perpendicular to the optic axis and the observation along the optic axis. Because of the finite width of the exciting line and of the 1 mm. separation used in the present case, the positive and negative components from two consecutive orders partly overlap. The extent to which the overlapping takes place depends on the orientation of the crystal. The Brillouin components in (d) are definitely broader than those in (b). For longitudinal scattering along the optic axis which corresponds to case (b) the calculated value of the shift of the Brillouin components = 2·59 cm.⁻¹ the separation of the successive orders being equal to 5 cm.⁻¹ The width of the unmodified line is 0·75 cm.⁻¹ For this case, therefore, the overlapping of the positive Brillouin component of one order and negative Brillouin component of the next higher order would be complete. For transverse scattering represented by case (c) the calculated value of the shift of the Brillouin components is 2·02 cm.⁻¹ The Brillouin components from two consecutive orders would therefore be adjacent to each other and appear as a single broad band The observed features of the interference patterns for different orientations of the crystal are thus qualitatively accounted for.

7. Infra-Red Spectra

Quartz is one of the few crystals most frequently examined in infra-red studies. The numerous investigations reported in the literature have already been reviewed by Saksena (1940). It was therefore thought unnecessary to summarise the existing infra-red data in the present paper. However, a

---

* Only the components due to the longitudinal sound waves in the crystal have been recorded. Those due to the two sets of transverse sound waves are not recorded owing to their comparatively feeble intensity

complete bibliography of the infra-red studies on quartz is appended to this paper.

The author takes this opportunity to express his respectful thanks to Professor Sir C. V. Raman for the loan of the quartz crystals and for his inspiring interest in the work. The author is also grateful to the authorities of the Annamalai University for the loan of the E3 quartz spectrograph employed in the present investigation.

8. SUMMARY

A detailed study has been made of the Raman effect in quartz using the λ 2536·5 mercury radiation as exciter The spectrum consists of 43 Raman lines, nearly half of them have been recorded for the first time Of these, fourteen Raman lines including two doublets constitute the internal oscillation spectrum of the unit cell of the quartz lattice. The frequency shifts of these have been very accurately determined Of the remaining 29 lines which constitute the second order spectrum of quartz, 17 have been satisfactorily explained as octaves and combinations of some of the principal frequencies The 12 Raman lines which are not explicable as combinations and overtones of the principal frequencies, constitute in part the super-lattice spectrum of quartz to be expected on the basis of the Raman theory of crystal dynamics

The specific heat of quartz has been evaluated on the assumption that the vibration spectrum consists of only 16 principal frequencies, 12 appearing in the Raman effect and 4 in the infra-red absorption The calculated values of the specific heat have been lower than the observed values over the range of temperature from $25 \cdot 8^\circ$ T to $803 \cdot 6^\circ$ T It is pointed out that the neglect of the super-lattice frequencies is responsible for the above discrepancy.

The Brillouin components due to longitudinal sound waves in quartz have been successfully photographed using an aluminised Fabry-Perot etalon The dependence of the form of the interference pattern on crystal orientation has been qualitatively accounted for on the basis of the variation of acoustic velocity with direction inside the crystal.

A complete bibliography on the Raman effect and infra-red studies in quartz is also appended.

REFERENCES

1. *Raman Effect*

Landsberg and Mandelstam	. *Naturwissenschaften*, 1928, 16, 557 ; *Comp. Rend*, 1928, 187, 109 ; *Zeit f Phys*, 1928, 50, 769
Krishnan, K S	*Nature*, 1928, 122, 477 ; *Ind Journ Phys*, 1929, 4, 131
Rao, I R.	. *Ind. Journ. Phys* , 1928, 3, 123
Pringsheim and Rosen	*Zeit f Phys* , 1928, 50, 741
Wood	*Phil Mag* , 1928, 6, 729.
Daure	*Ann de Physique*, 1929, 12, 375
Gross and Romanova	*Zeit. f Phys* . 1929, 55, 744
Nisi	. *Proc Imp Acad (Tokyo)*, 1929, 5, 127
Rasetti	*Nuovo Cimento*, 1932, 9, 72
Kujumzelis	*Zeit f Phys* , 1935, 97, 561 ; 1936, 100, 221
Nedungadi	*Proc. Ind Acad Sci* , A, 1940, 11, 86
Saksena	*Ibid* , 1940, 12, 93
Roop Kishore	*Ibid* , 1942, 16, 36.
Landsberg and Leontowitsch	*Zeit f Phys.*, 1929, 53, 439
Brickwedde and Peters	*Phys. Rev* , 1929, 33, 116
Landsberg and Mandelstam	*Zeit f Phys* , 1929, 58, 250 ; 1930, 60, 364
Ney	*Ibid* , 1931, 68, 554
Ornstein and Went	*Physica*, 1935, 2, 503
Went	*Doctorate Thesis, Utrecht, 1935*
Raman and Nedungadi	*Nature*, 1940, 145, 147
Venkateswarln	*Proc. Ind Acad Sci* , A, 1941, 14, 529.
Cabannes	*Comp Rend* , 1929, 188, 249
Menzies	*Phil. Mag* , 1929, 8, 504
Bouhet	. *Comp Rend* , 1937, 204, 1661
Cabannes and Bouhet	*Ibid.*, 1937, 205, 768
Michalke	. *Zeit. f. Phys* , 1938, 108, 748
Weiler	*Helv. Phys Acta* , 1932, 5, 302 ; *Nature*, 1932, 130, 893 ; *Zeit. f. Phys* , 1933, 80, 617
Krishnan, R. S.	.. *Nature*, 1945, 155, 452.
Saksena	*Proc Ind Acad Sci* , A, 1942, 16, 270

2 *General*

Krishnan, R S	. *Proc Ind Acad Sci* , A, 1945, 22, 182
Norris	.. *Ibid* , 1941, 14, 499
Herzberg	*Raman and Infra-red Spectra of Polyatomic Molecules*, New York, 1945.
Raman, C. V	*Proc. Ind Acad Sci* , 1943, 18, 237.

3. *Infra-red*

Merritt	. *Wied. Ann.*, 1895, 55, 49
Bormann	. *Zitt Verst. Kon. Akad. Wet. Amsterdam*, 1896, 43, 8, 1896
Nichols	*Wied. Ann.*, 1897, 60, 401.

Rubens and Nichols	*Phys. Rev.*, 1897, **4**, 314.
Rosenthal	*Wied. Ann.*, 1899, **68**, 783.
Rubens	*Phys. Zeit*, 1903, 4
Coblentz	*Phys Rev.*, 1906, **23**, 125 ; *J. Franklin Institute*, 1914, **177**, 445 , *Bull. Bur. Stds.*, 1914, **11**, 471.
Reinkober	*Ann. Phys.*, 1911, **34**, 343
Liebisch and Rubens	*Preus. Akad. Wiss Phys Klasse*, 1919, 198.
Dreisch	*Zeit. f. Phys.*, 1927, **42**, 426.
Reinkober and Kipcke	*Ibid*, 1928, **48**, 205.
Plyler	*Phys. Rev.*, 1929, **33**, 48.
Czerny	*Naturwissenschaften*, 1929, **17**, 12 ; *Zeit. f. Phys*, 1929, **53**, 317.
Mcginnety	*Proc. Univ. Durham Phil. Soc.*, 1931, **8**, 337.
Drummond	*Nature*, 1932, **130**, 928 , 1934, **134**, 739 ; 1936, **138**, 248 ; *Proc. Roy. Soc.*, 1936, **153**, 328.

DESCRIPTION OF PLATES

PLATE XI

Fig. 1   Raman spectrum of crystalline quartz taken with the El spectrograph.

Fig. 2   Its microphotometric record.

PLATE XII

Fig. 4a. The microphotometric record of the Raman spectrum of quartz taken with the E3 spectrograph.

Fig. 4b. The microphotometric record of the mercury spectrum.

PLATE XIII

Fig. 3a. The Raman spectrum of quartz taken with E3 spectrograph (heavily exposed photograph).

Fig. 3c   Do. (lightly exposed photograph).

Fig. 3b. The comparison spectrum of the mercury arc.

Fig. 5a & e.   The interference pattern of the 2536 5 line of mercury.

Fig. 5b, c & d.   The interference patterns of the same radiation scattered by a crystal of quartz showing the Brillouin components for three different orientations.

1228·0
1159·3
1081·9
1063·7
λ 2603·2

805·8
794·7

696·4

λ 2576·3

508·8
488
466·0
452·2
λ2563·9
403·8
394·8
357·2

266·1
240
206·4

170
145
127·7

λ2536·5

1228·0
1159·3
1081·9
1063·7
λ·2603·2

805·8
794·7

696·4

508·8
488
466·0
452·2
403·8
394·8
357·2

266·1
240
206·4
170
145
127·7

λ2536·5

Fig. 1   Fig. 2

λ 2536 6

277
45
805 4
866

357 2
399 8
403 6
452 2
466 0
488
508 8

696 4

794 7
805 8

063 7
081 9
1159 3
228 0

39

448
430

644

730

848
422
924

1044

1068
1086

1394
1444
1475

1596
1630

2128
1888
1864

2424

F 4

2536 5Λ
2531 1Λ

Fɪɢ. 3

Fɪɢ. 5

CHEMISTRY OF THE THIAZOLES

Part I. Synthesis of 5-Aminothiazole Derivatives

By K. GANAPATHI AND (MRS.) ALAMELA VENKATARAMAN

(From the Department of Chemotherapy, Haffkine Institute, Parel, Bombay)

Received July 28, 1945

(Communicated by Lt.-Col. S. S. Sokhey, M.A., M.D., F.A.SC., I.M.S.)

1. Introduction · Previous Work

FOR the synthesis of the 4- and 5-sulphanilamido derivatives of thiazole, we required 4-aminothiazole, 5-aminothiazole and their various substitution products Though 2-aminothiazole has been synthesised as early as 1889, the isomeric 4-amino and 5-aminothiazoles are not known so far. However a number of derivatives have been described in literature whose structures have not been established beyond doubt. Wallach[1] obtained a compound called " chrysean " by passing hydrogen sulphide into a concentrated solution of sodium cyanide Later on, Hellsing[2, 3] investigated this compound and suggested it to be probably 2-thioamido-5-amino-thiazole; on degrading this, he obtained an acetamino compound, m.p. 162°, which he has suggested to be 5-acetaminothiazole Another series of compounds have been prepared by Weidel and Niemilowicz[4] by the degradation of " ethylenethiouramil"; as the final degradation product he obtained a compound described as 2-methyl-5-aminothiazole, which being obtained in very small quantities was not further investigated Apart from these, there is on record no other attempt made to synthesise 5-aminothiazole or its derivatives. Our preliminary studies led us to realise that the synthesis of these compounds requires a thorough investigation and so all the methods theoretically possible were tried in suitable cases. In this paper is presented some of the results obtained and ready for publication

2 Conversion of Thiazole-5-Carboxylic Esters into 5-Aminothiazole Derivatives

The conversion of the thiazole carboxylic esters into the aminothiazoles was first tried because all the starting esters required are known and can be prepared comparatively easily; they are all of unequivocal constitution and so the structures of aminothiazole and derivatives prepared from them will be definite and could be used as reference compounds for further studies. The three methods known for the conversion of the ester into the

343

A1

amino grouping, *viz.*, the Hofmann, the Curtius and the Schmidt's reactions
were tried with the easily accessible ethyl 2:4-dimethylthiazole-5-carboxylate.
The amide of the thiazole ester could not be converted into the amino com-
pound by using sodium hypochlorite or sodium hypobromite under a variety
of conditions; the use of alkali caused decomposition of the starting product
and about 50 per cent of the amide was also hydrolysed to the acid. Hydra-
zoic acid failed to react with 2:4-dimethylthiazole-5-carboxylic acid or its
ester. (Similarly, 2-amino-4-methylthiazole-5-carboxylate and 2-sulpha-
nilamido-4-methylthiazole-5-carboxylic acid failed to react with hydrazoic
acid.) The Curtius reaction yielded the amino compound under a particular
set of conditions. The hydrazide obtained from the ester on treatment with
nitrous acid furnished in good yields the liquid azide which reacted with
alcohol to yield the urethane (I) This could not successfully be converted
into the amine; it resisted hydrolysis with 48 per cent. hydrobromic acid,
concentrated hydrochloric acid and 50 per cent sulphuric acid but was
completely decomposed with 10 per cent sodium hydroxide. The stability
of this urethane to acids and its instability to alkali is characteristic of the
thiazoles. The decomposition of the azide with various other reagents was
studied. While the treatment with 50 per cent acetic acid (Lindeman)[7]
produced a high melting product difficult to purify, dilute hydrochloric acid
furnished a small quantity of the required 2:4-dimethyl-5-aminothiazole
(II, R=H) With dioxane,[8] the azide decomposed to yield the urea deriva-
tive (III) along with liquid product not identical with the amine Treat-

Me C——N   Me·C——N   N——C·Me   Me·C——N
‖   ‖   ‖   ‖   ‖   ‖   ‖   ‖
EtO₂C·NH C   C·Me   R·NH·C   C·Me   Me·C   C·NH·CO NH·C   C·Me
       \ /   \ /   \ /   \ /
        S   S   S   S
       (I)   (II)   (III)
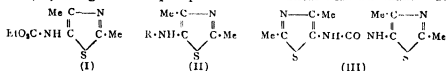
ment of the azide with acetone did not lead to its decomposition When
the *dry* azide was treated with a mixture of acetic acid and acetic anhydride,
2:4-dimethyl-5-acetaminothiazole (II, R=Ac) was obtained in practically
quantitative yields, the urea derivative being absent It appears that in
this case as the amine is being formed it is fixed up immediately as the acetyl
derivative so that the intermediate isocyanate is not given a chance to react
with it to form the urea derivative. The acetamino compound under the
conditions described in the experimental part underwent hydrolysis
to furnish 2:4-dimethyl-5-aminothiazole.

Ethyl 4-methylthiazole-5-carboxylate was next chosen for study and
the behaviour of this compound was not quite similar to that of the 2:4-
dimethyl analogue. Though the corresponding amide,[9] with sodium hypo-
chlorite or sodium hypobromite, under the usual conditions, underwent

decomposition, under a set of conditions[10] yielded the required 4-methyl-
5-aminothiazole (IV, R=H), isolated, after acetylation, as the acetyl deri-
vative (IV, R=Ac). The decomposition of the corresponding azide with
various reagents was also tried. The urea derivative (V) could readily be
obtained by treating the azide with water. With dilute hydrochloric acid
no amine could be isolated. With acetic acid and acetic anhydride, the
azide furnished 4-methyl-5-acetaminothiazole (IV, R = Ac) in good yields.
The hydrolysis of this to the amino compound could not successfully be
effected. While under the usual conditions the product remained unaffected,
under drastic conditions it underwent extensive decomposition.

$$
\begin{array}{cccc}
\underset{\text{(IV)}}{\underset{\displaystyle\parallel}{\text{Me·C}}\!-\!\!-\!\text{N}} &
\underset{\text{(V)}}{\text{N}\!-\!\!-\!\text{C·Me}} &
\underset{\text{}}{\text{Me·C}\!-\!\!-\!\text{N}} &
\underset{\text{(VI)}}{\text{Me·C}\!-\!\!-\!\text{N}}
\end{array}
$$
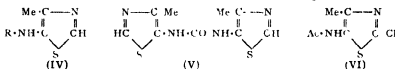
To study the influence of the various groupings in position 2 of the
thiazole ring on the nature of the decomposition of the azide, some more
thiazole derivatives were investigated. Ethyl thiazole-5-carboxylate could
not successfully be converted into 5-acetaminothiazole so far. Starting
from ethyl 2-chloro-4-methylthiazole-5-carboxylate we could obtain 2-chloro-
4-methyl-5-acetaminothiazole (VI) though in the decomposition of the azide
with acetic acid and acetic anhydride the yield of the acetamino compound
is not so good in this case. Ethyl 2-bromothiazole-5-carboxylate could
not be converted into 2-bromo-5-acetaminothiazole, the decomposition of
the azide was not at all smooth as would be observed. The hydrazide (VII)
obtained from ethyl 2-aminothiazole-5-carboxylate was treated with nitrous
acid. Since in this compound the 2-amino group does not undergo diazo-
tization under the conditions employed, the azide (VIII) was produced in
good yields; this with acetic acid and acetic anhydride yielded 2:5-diace-
tamino thiazole (IX) which is required as a reference compound in connection
with studies on orientation in the thiazole series. Starting from ethyl 2-amino-

$$
\begin{array}{ccc}
\underset{\text{(VII)}}{\text{NH}_2\text{NH·CO·C}\!-\!\!-\!\text{N}} &
\underset{\text{(VIII)}}{\text{N}_3\text{CO·C}\!-\!\!-\!\text{N}} &
\underset{\text{(IX)}}{\text{AcNH·C}\!-\!\!-\!\text{N}}
\end{array}
$$

$$
\underset{\text{(X)}}{\text{R·NH·C}\!-\!\!-\!\text{N}}
$$
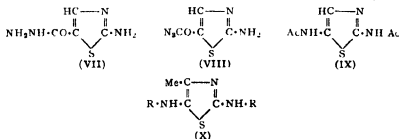
4-methylthiazole-5-carboxylate, we obtained 2 : 5-diacetamino-4-methylthia-
zole (X, R=Ac); in this case, however, the treatment of the azide with dilute

hydrochloric acid furnished in good yields a product whose nitrogen value was much lower than that of the expected amine (X, R = H).

3   Conversion of 5-Acetylthiazoles into 5-Acetaminothiazoles

In the benzene and other polycyclic series, the conversion of the acetyl into the acetamino group by the Beckmann transformation of the oxime has been achieved with notable success. So we tried this reaction on the oximes of the two 5-acetyl derivatives of thiazole known and prepared without difficulty. On treating the oxime of 4-methyl-5-acetylthiazole[12] with phosphorous pentachloride in benzene we were able to obtain in about 30 per cent. yields 4-methyl-5-acetaminothiazole, m.p. 86–87°, which was identical with the product obtained from ethyl 4-methylthiazole-5-carboxylate. On the other hand, treatment of the oxime with hydrogen chloride and acetic anhydride, a condition very often employed, led to the production of not the acetamino compound but a crystalline product, m.p. 73°, which was found to be the acetyl derivative of the oxime. This acetyl derivative on hydrolysis yielded the original oxime. This oxime of 2 : 4-dimethyl-5-acetylthiazole[11] on treatment with phosphorous pentachloride furnished in about 10 per cent. yields 2 : 4-dimethyl-5-acetaminothiazole. Treatment of this oxime with hydrogen chloride and acetic anhydride yielded an oil which on hydrolysis yielded back the oxime; this oily product is therefore the acetyl derivative of the oxime.

4   Synthesis of 5-Nitrothiazoles and Their Reduction to 5-Aminothiazoles

The synthesis of 5-aminothiazole derivatives by the reduction of the corresponding nitrothiazoles was then investigated. It is indeed strange that upto 1938, no nitrothiazole compound was known. Ochiai[13] first prepared 2-hydroxy-4-methyl-5-nitrothiazole   and   2-nitroamino-4-methyl-5-nitrothiazole by nitrating 2-hydroxy-4-methylthiazole   and   2-amino-4-methylthiazole respectively. He could not reduce the two nitrothiazoles to the corresponding amino compounds. Nagasawa[14] has subsequently prepared 2 : 4-dimethyl-5-nitrothiazole   and   2-acetamino-4-nitro-5-methylthiazole by nitration. The original papers of these authors are not available and the abstract of these contain very little details of the experiments. To prepare 4- or 5-nitrothiazole we planned to start with a 2-halogeno, amino or acetaminothiazole (2-hydroxythiazole is as yet unknown), nitrate and then convert the halogeno or the amino group into the hydrogen atom. Our attempts to nitrate 2-chloro and 2-bromothiazole (even at 100° with excess of nitric acid and sulphuric acid) ended in failure, the starting compound being

recovered unchanged. This is not unexpected because thiazole itself undergoes bromination only in the vapour phase[15] and the speed of substitution by kationoid reagents in the case of chlorothiazole is far slower than in the case of thiazole because of the "inductive effect (I)" of the halogen atom.[1a] 2-Acetaminothiazole on the other hand, as was expected, easily underwent nitration to yield a mono nitration product. Ochiai and Nagasawa[17] have concluded from their studies that a substituent as hydroxy, methyl and amino at the position 2 of the thiazole ring directs the incoming substituent (in kationoid substitution) to the position 5. Their conclusion is unwarranted because in all cases studied by them there is already a methyl group blocking the position 4. Erlenmeyer, Bloch and Kiefer[18] have mentioned that the sulphonation of 2-aminothiazole leads to 2-aminothiazole-5-sulphonic acid; the proof for this structure they had promised in a subsequent paper which has not so far appeared. Bogert and Cherbcoff[19] obtained a dye by coupling diazotised *para* nitraniline (and also sulphanilic acid) with 2-aminothiazole in which they have assumed, without giving any proof, that the azo group is linked to the position 5 of thiazole nucleus Though in substitution by kationoid reagents, it is very likely that a group in position 2 will direct the incoming substituent to the position 5 if it is unoccupied (and to position 4 if position 5 is occupied), a definite proof for this is lacking. Our attempts to obtain this so far are unsuccessful. We are thus tentatively assigning the structure of 2-acetamino-5-nitrothiazole to the compound obtained by nitrating 2-acetaminothiazole. Hydrolysis of this furnished 2-amino-5-nitrothiazole which could also be prepared directly from 2-aminothiazole by nitration and rearrangement as in the case of 2-amino-pyridine. All attempts to convert the 5-nitro-2-amino and nitro-acetamino compounds into the diacetaminothiazole by reduction and acetylation ended in failure Though the reduction of the nitro compound proceeded on with a number of reducing agents, the isolation of the diacetamino compound (which we have synthesised independently by other method for comparison) was not possible. The only slender evidence we can advance at present to show that the nitro group occupies the position 5 is that the picrate of the reduction product from 2-amino-nitrothiazole is not identical with the picrate of 2 : 4-diaminothiazole.[20] By an alternative method, an attempt was made to synthesise 2-amino-5-nitrothiazole and 2-amino-4-nitrothiazole for reference by nitrating 2-acetaminothiazole-4-carboxylate and 2-acetamino-thiazole-5-carboxylate respectively, hydrolysing and then decarboxylating the products obtained. But the nitration of the two compounds did not at all proceed on, the starting material being recovered unchanged.

2 : 4-Dimethylthiazole furnished on nitration 2 : 4-dimethyl-5-nitrothia-zole in good yields. Though the reduction of this nitro compound with

all the usual reducing agents undoubtedly proceed on, the isolation of the reduction product once again presented difficulties. Under the conditions described in the experimental part, by using iron, we could isolate, after acetylation, 2:4-dimethyl-5-acetaminothiazole in about 25 per cent. yield. We have got on hand the reductions of some nitrothiazole derivatives.

5. SYNTHESIS OF 5–AZOTHIAZOLES AND THEIR REDUCTION TO 5–AMINOTHIAZOLES

The preparation of the amino compound by the reduction of the corresponding azo compound was successful in one case attempted but this method is only of limited applicability. 2:4-Dimethylthiazole or 2-amino-4-methylthiazole did not couple with diazotised *para* toluidine. 2-Hydroxy-4-methylthiazole could not be nitrosoated but it underwent coupling with diazotised *para* toluidine yielding the azo dye (XI). While this decomposed on treatment with tin or stannous chloride and hydrochloric acid, sodium hydrosulphite smoothly reduced it to 2-hydroxy-4-methyl-5-aminothiazole (XII) which, as is to be expected, is feebly basic.
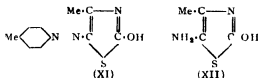
6. SOME UNSUCCESSFUL ATTEMPTS

The bromine atom in position 2 of thiazole is very reactive and could be converted into amino and substituted amino groups.   But the bromine atom at the position 5 exhibits the properties of that attached to the benzene ring. 2:4-Dimethyl-5-bromothiazole was not at all reactive towards potassium phthalimide, urotropin and sulphanilamide   It did not form the Grignard reagent under the standard conditions, though it was debrominated by zinc dust and acetic acid   Huntress and Pfister[31] have also found the chlorine atom in 2-phenyl-5-chloro-4-hydroxymethyl thiazole to be very unreactive.

2:4-Dimethylthiazole did not react with hydrazoic acid to form 2·4-dimethyl-5-aminothiazole

An attempt to synthesise 2-methyl-5-aminothiazole by the Gabriel's method[22] by treating acetylglycineamide with phosphorous pentasulphide as shown below was not successful. Acetylglycineamide appears to decompose
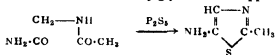
into acetamide, the smell of which is very predominant, under the conditions of the reaction.

7. EXPERIMENTAL

Ethyl 2 : 4-dimethylthiazole-5-carboxylate.—By reacting thioacetamide (25 g.) with ethyl α-chloroacetoacetate (55 g.), 50 g. (82% yield) of the thiazole carboxylic ester was obtained. The following method does not require the isolation of thioacetamide and is very rapid: A mixture of acetamide (59 g.) and phosphorous pentasulphide (45 g.) in benzene (50 c.c.) was gently warmed on the steam-bath and treated gradually with a solution of ethyl α-chloroacetoacetate (33 g.) in benzene (50 c.c.), heating being discontinued during the addition of the ester. After refluxing the mixture for 3 hours more, it was cooled, the gummy mass dissolved in water and acidified with hydrochloric acid (50 c.c.). The acidic aqueous layer was separated, extracted with ether, neutralised with solid sodium carbonate and the oily layer obtained steam-distilled. The distillate furnished 25 g. of the crystalline ester. This was further purified by dissolving it in dilute hydrochloric acid, extracting the solution with ether and then reprecipitating with sodium carbonate (charcoal). The product thus obtained was very pure; m p 50–51° The original benzene layer yielded a little more of the ester

2 : 4-Dimethylthiazole-5-amide.—Ethyl 2 : 4-dimethylthiazole-5-carboxylic ester (14 g.) was shaken with excess of liquor ammonia (350 c.c.) and allowed to stand overnight when most of the solid went into solution. A small quantity of the undissolved ester was filtered off and the clear solution evaporated to a small volume when the amide separated. It was filtered and crystallised from a small quantity of water (yield, 6 6 g.), m.p. 73–74° (Found: N, 17·77; $C_6H_8O_4N_2S$ requires N, 17·64%). The mother-liquor on evaporation to dryness furnished the acid, m.p 227° (3 g.) produced by the hydrolysis of the ester.

2 : 4-Dimethyl-5-acetaminothiazole (II, R=Ac).—A mixture of 2 : 4-dimethylthiazole-5-carboxylate (18 5 g.), hydrazine hydrate (22 c.c. of 40%) and alcohol (15 c c) was refluxed for 3 to 4 hours on the steam-bath The alcohol was distilled off under reduced pressure, the residue dissolved in ice-water, the aqueous solution extracted with ether to remove any unchanged ester and evaporated to dryness (yield of the hydrazide, 16 g.). On crystallisation from excess of boiling benzene it had m.p 139–40°. The crude hydrazide (8·5 g.) as obtained above dissolved in dilute acetic acid (75 c.c. of 1 :3) was treated with a solution of sodium nitrite (4·5 g) in water (15 c.c.) at 0° C. The azide, which was crystalline at low temperature, was taken up in ether and dried over anhydrous sodium sulphate. The ethereal solution was added to a mixture of acetic acid (10 c.c.) and acetic anhydride

(15 c.c.). After removing the ether, the residue was gently warmed until the evolution of nitrogen was complete. It was then concentrated to a small volume by distillation and the residue dissolved in a small quantity of ice-water (50–75 c.c.). The decolourised solution was carefully neutralised with solid sodium carbonate when the acetamino compound separated in a crystalline form. This was filtered, washed with a little water and dried; yield, 8·4 g. (99%). On crystallisation from benzene or a small volume of water it separated in thick plates and had m.p. 64–65° (Found : N, 16·70; $C_7H_{10}ON_4S$ requires N, 16·46%) The acetamino compound yields a picrate, m.p. 210°.

The above described acetamino compound (10 g.) was refluxed with alcohol (25 c.c.), concentrated hydrochloric acid (10 c.c.) and water (2 c.c.) for 10 hours. More alcohol (25 c.c.) was added and the solution concentrated to a small bulk under reduced pressure. The residue was diluted with a few bits of ice, covered with ether and basified with 40% caustic soda. The free amino compound was recovered through ether extraction. This yielded 6·8 g. (theory 7·4 g.) of the crude 2 : 4-dimethyl-5-aminothiazole; b.p. 130–150°/3–5 mm The amino compound yielded a picrate, m.p. 189–91°

Urea derivative (III).—On crystallisation from alcohol it separated in plates and had m.p. 246–48° (Found : N. 20·38; $C_{11}H_{14}N_4O_2$ requires N. 19·85%).

2 : 4-*Dimethylthiazole-5-urethane (I)*.—The ethereal solution of the azide described above obtained from the hydrazide (4·0 g.) was refluxed with absolute alcohol (25 c.c.) for 1 hour. On distilling off the solvent, the urethane was obtained as a colourless mass (yield, 3·3 g.) On crystallisation from benzene it melted at 96–97° (Found : N, 14·34; $C_8H_{12}O_2N_2S$ requires N, 13·99%) The picrate of the urethane melted at 184–85°.

4-*Methyl-5-acetamidothiazole   (IV, R=Ac.)*.—(i)   4-Methylthiazole-5-carboxylic hydrazide[35] (3·5 g.) dissolved in dilute hydrochloric acid (8·5 c.c. of concentrated acid diluted with 25 c.c. water) was treated with a solution of sodium nitrite (1·8 g.). The azide separated immediately as a crystalline mass, which was filtered, washed with a little ice-cold water and air-dried (yield, 3 g.) It crystallised from ether in fibrous prismatic needles, m.p. 83°. The azide was dissolved in a mixture of acetic acid (3 c.c.) and acetic anhydride (5 c.c.) and gently warmed till the evolution of nitrogen ceased. The reaction mixture was concentrated and diluted with cold water when the acetamino compound separated as a crystalline solid (yield, 3·2 g.): it crystallised from boiling water or benzene in fine needles and had m.p. 87° (Found : N, 17·78; $C_6H_8N_2OS$ requires N, 17·94%).

(ii) **4-Methylthiazole-5-carboxylamide** (2·6 g.) was treated with potassium hydroxide (40 c.c. of 2 5 N) to which had been added under ice-cooling bromine (1 c.c.). The mixture was allowed to stand at the room temperature for 2 days and then extracted with ether The ethereal extract, which showed fluorescence, was evaporated to dryness and treated with a few drops of acetic anhydride The acetyl derivative thus obtained (0·6 g.) crystallised from water in silky needles and had m.p 87° causing no depression with the specimen reported above The picrate of this acetamino compound, crystallised from hot methanol, had m.p 198°.

Urea derivative (*V*)—The azide obtained as described above under (i) was gently boiled with water for 3 hours; the solid that separated was filtered and crystallised from boiling alcohol; m.p 244–47° (Found : N, 21·61; $C_8H_{10}ON_4S_2$ requires N, 22·02%) The urea derivative is also obtained in good yields by boiling the azide with benzene moistened with a few drops of water

2-Chloro-4-methyl-5-acetaminothiazole (*VI*)—A mixture of ethyl 2-chloro-4-methylthiazole-5-carboxylate[12] (6 0 g.) and hydrazine hydrate (6 c.c. of 42%) and alcohol (10 c c) was refluxed for 4 hours More alcohol was added to dissolve the crystals, the solution filtered hot and cooled. The yellow crystals were separated and dried; m.p. 184° (yield, 4·7 g.) The above crystalline hydrazide (3·1 g.) dissolved in water (25 c.c.), acidified with concentrated hydrochloric acid (5 c.c.) and treated with a solution of sodium nitrite (1·3 g.). The azide that formed was quickly filtered, washed and air-dried (yield, 1·8 g.); m p. about 115° This was dissolved in acetic acid (5 c.c.) and acetic anhydride (3 c.c), gently warmed and then heated on the steam-bath for 1 hour On working up as usual, the acetamino compound was obtained (yield, 0·6 g.) On crystallisation from alcohol (charcoal) it had m p. 196–97° (Found · N, 14 54 . $C_6H_7N_2OS$ Clrequires N, 14·70%).

2 : 5-Diacetaminothiazole (*IX*)—Ethyl 2-aminothiazole-5-carboxylate (3 g.) was converted into the hydrazide (m.p. 205°) (2·5 g) as usual It was taken up in dilute acetic acid and converted into the azide (2·3 g.) which on treatment with acetic acid and acetic anhydride yielded the acetamino compound, (2·1 g.). From glacial acetic acid it was obtained as an amorphous powder not melting below 285° (Found : N, 20·93; $C_7H_9N_3O_2S$ requires N, 21·09%).

4-Methyl-2:5-diacetaminothiazole (*X, R=Ac*).—Ethyl 2-amino-4-methyl-thiazole-5-carboxylate (4·2 g.) in alcohol (15 c.c.) was refluxed with hydrazine hydrate (15 c.c. of 42%) for 14 hours. The hydrazide that precipitated

was filtered off, washed with alcohol and recrystallised from boiling water;
m.p. 211–13° (yield, 2·2 g.). From the alcoholic filtrate the unchanged ester
could be recovered. The hydrazide (2·1 g.) was converted into the aceta-
mino compound through the azide as described above and crystallised from
boiling water (charcoal); it separated in thick rhombic plates and
did not melt below 240° (yield, 2·1 g) (Found: N, 19·68; $C_8H_{11}O_2N_3S$
requires N, 19·71%).

Urea derivative.—The azide prepared as described above was refluxed with
water for 2 hours and the product obtained crystallised from dilute acetic
acid; m.p. 240–45°. (Found: N, 28·89; $C_9H_{13}N_6OS_2$ requires N, 29·56).

2-Acetamino-4-methyl-5-urethanylthiazole.—The   azide   as   described
above was refluxed with alcohol and the urethane obtained (m.p. 150–55°)
was acetylated by treating with acetic anhydride. On crystallisation from
dilute alcohol, the acetyl derivative of the urethane melted at 203° (Found·
N, 17·26; $C_9H_{13}N_3O_3S$ requires N, 17·28%). The picrate of the urethane
on crystallisation from hot water had m.p. 208°.

Oxime of 4-methyl-5-acetylthiazole.—A mixture of 4-methyl-5-acetyl-
thiazole[12] (5 g.) in alcohol (10 c c.), hydroxylamine hydrochloride (4 g.) and
sodium acetate (8 g.) in water (10 c.c.) was refluxed for 3 hours   The oxime
crystallised out on cooling in thick glistening rhombic prisms.   The mixture
was diluted with ice-water, the crystals filtered, washed and dried (yield,
5·4 g.).   On crystallisation from hot alcohol or excess boiling benzene it
separated in thick plates and had m.p. 145°   (Found: N, 17·65; $C_6H_8ON_2S$
requires N, 17·94%)   On using pyridine in the place of sodium acetate and
alcohol, the same oxime was obtained in about the same yield.   The picrate
of the oxime, crystallised from boiling alcohol, had m.p. 166°.

Action of phosphorous pentachloride on the oxime.—The above described
oxime (finely powdered, 1 g.) suspended in dry benzene (30 c.c.) was treated
with powdered phosphorous pentachloride (1 g.). The mixture was vigorously
refluxed for 30 minutes and the solvent removed completely under reduced
pressure.   The residue was dissolved in ice-water (charcoal), filtered and
neutralised with sodium carbonate. The acetamino compound separated
as a crystalline solid which was filtered, dried and extracted with benzene
to free it from the inorganic material.   The benzene extract yielded 0·3 g.
of the compound (m p. 86–87°) (picrate m p. 198°) found to be identical
with 4-methyl-5-acetaminothiazole

Action of acetic anhydride and hydrogen chloride on the oxime.—The
oxime described above (3 g.) in acetic anhydride (30 c.c.) was saturated with
dry hydrogen chloride and allowed to stand overnight. Most of the acetic

anhydride was distilled· off and the residue dissolved in a small volume of water. On neutralising the clear solution with sodium carbonate, a crystalline white solid separated which was separated and crystallised from ether (yield, 2·8 g.). On recrystallisation from ligroin it separated in thick rectangular blocks and had m.p. 73° [Found: N, 13·86; $C_8H_{10}O_2N_2S$ (acetyl derivative of the oxime) requires N, 14·14%]. This was found to be the acetyl derivative of the oxime and on hydrolysis with dilute hydrochloric acid yielded back the original oxime, m p 145°

2:4-*Dimethyl*-5-*acetylthiazole.*—This compound has been obtained by Smith and Sapiro[11] in poor yields. But we could prepare it in good yields by the following two methods:

(i) A solution of chloroacetylacetone (9·0 g.) in alcohol (10 c.c.) was treated with thioacetamide (5 g.) under cooling in ice-bath; it was then allowed to stand at the room temperature for 15 minutes and then heated on the steam-bath for 15 minutes more On cooling, crystals of 2·4-dimethyl-5-acetylthiazole hydrochloride separated which on working up yielded the free base, b.p 228–30° (yield, 10 g.)

(ii) A mixture of acetamide (30 g.) and phosphorous pentasulphide (22·5 g.) was gently warmed on the water-bath and treated with chloroacetyl-acetone (13·5 g.) in small quantities. The mixture was carefully warmed for 15 to 20 minutes. The reaction product was dissolved in water (120 c c.), acidified with concentrated hydrochloric acid (25 c.c.), extracted with ether and the acidic solution after basification was thoroughly extracted with ether From the ether extract 2 . 4-dimethyl-5-acetylthiazole was obtained, b p 230° (yield, 10 g.).

Oxime.—By treating the foregoing acetylthiazole derivative with hydroxylamine hydrochloride and sodium acetate in alcohol the oxime was obtained which on crystallisation from dilute alcohol or boiling benzene had m.p. 131°. (Found: N, 16·72; $C_7H_{10}N_2OS$ requires N, 16 46%). The oxime yielded a picrate, m.p. 184–85°.

Treatment of the oxime with phosphorous pentachloride.—The oxime (1 g.) suspended in dry benzene (25 c c.) was treated with phosphorous pentachloride (1 g.) and working up as usual, 0 15 g. of 2: 4-dimethyl-5-acetamino-thiazole (m.p. 62–64°) was obtained.

Action of acetic anhydride and hydrogen chloride on the oxime.—On treating the foregoing oxime with acetic anhydride and hydrogen chloride and working up as usual, an oily product (picrate, m.p. 122–24°) was obtained which on hydrolysis with dilute hydrochloric acid, yielded back the original oxime, identified as such and also as the picrate.

2-Acetamino-5-nitrothiazole.—2-Acetaminothiazole (50 g.) in concentrated sulphuric acid (150 c.c.) was treated with fuming nitric acid (15 c.c.) below 10°; the mixture was heated on the steam-bath for about 15 minutes (or allowed to stand overnight) and poured into crushed ice. The copious precipitate formed was filtered, washed thoroughly with ice-water and dried at 100° (yield, 54–58 g.). On crystallising from acetic acid or alcohol, it was obtained in long plates and had m.p. 265° (Found: N, 22·20; $C_5H_5O_4N_3S$ requires N, 22·46%). The nitro compound dissolves in alkali and ammonia with a deep orange colour

2-Amino-5-nitrothiazole.—The foregoing acetyl compound (54 g) was hydrolysed by boiling with hydrochloric acid (500 c.c. of 4 N) until solution was complete. The red solution was diluted with an equal volume of water, boiled with charcoal (10 minutes) and the amino compound precipitated from the clear solution by adding crystalline sodium acetate. The crystalline yellow precipitate was filtered, washed with water and dried (yield, 34 g.) It crystallised from alcohol or boiling water in groups of deep yellow needles, m.p. 203° (Found: N, 28 83: $C_3H_3O_2N_3S$ requires N, 28·96%) It yielded a picrate, m.p. 190–91°

This compound can also be prepared directly from 2-aminothiazole as follows· Crystalline 2-aminothiazole (20 g.) was added to concentrated sulphuric acid (50 c.c.) below 15° C. followed by fuming nitric acid (10 c.c.) The reaction mixture was left aside without external cooling when the temperature rose to 45° After allowing to stand overnight it was poured into crushed ice (about 500 g.), filtered from dark impurity and the clear filtrate neutralised with solid sodium carbonate The nitro compound separated as a crystalline solid (yield, 20–21 g.) On crystallisation from boiling water (charcoal) it yielded 18·5 g of 2-amino-5-nitrothiazole, m.p 200–01°

2-Acetamino-4-methyl-5-nitrothiazole.—2-Acetamino-4-methylthiazole (10·4 g.) in concentrated sulphuric acid (30 c.c.) was treated with fuming nitric acid (3 c.c.) below 10°. The reaction mixture after allowing to stand at the room temperature overnight was poured into ice and worked up as described above. The nitro compound (13 g.) on crystallisation from dilute acetic acid separated in pale yellow elongated rods, m.p. 228° (Found: N, 20·64. $C_6H_7O_3N_3S$ requires N, 20·89%)

2-Amino-4-methyl-5-nitrothiazole.—The foregoing acetamino compound was hydrolysed as described in the previous experiment. The amino compound obtained on crystallisation from alcohol had m.p. 220° (Found: N, 26·15; $C_4H_5O_2N_3S$ requires N, 26·40%). Picrate of this crystallised from hot alcohol and had m.p. 180°.

2 : 4-*Dimethyl-5-nitrothiazole.*—This compound has been described by Nagasawa[16] but no details of the preparation are available. The following condition has been found to furnish it in practically quantitative yields: 2 : 4-dimethylthiazole (22·6 g.) was added with cooling to a mixture of concentrated sulphuric acid (50 c.c.) and fuming nitric acid (40 c.c.). The reaction mixture was warmed at 60–70° for 3 hours and finally on the boiling water-bath until the evolution of fumes stopped (10 hours). After cooling, the mixture was poured into powdered ice (300 g.) when part of the nitro compound separated as crystalline solid. Sodium acetate was added to the mixture until no more of the nitro compound separated. It was taken up in ether, the extract dried and the solvent removed. On fractionation of the residue (30 g.), 2 : 4-dimethyl-5-nitrothiazole passed over at 170–80°/6 mm. or 100–01° at 1·5 mm. (yield, 22–25 g.) Nagasawa gives b.p. 65°/0 07 mm.

2 : 4-*Dimethyl-5-acetaminothiazole.*—2 : 4-Dimethyl-5-nitrothiazole (5 g.) in benzene (150 c c.) was refluxed with activated iron (50 g.)[34] for 7 hours, about 15 c.c. of water being added gradually during this period. The benzene layer was decanted off, the residue washed with boiling benzene (30 c.c.) and the solvent distilled off. The residue (3 6 g.) was boiled with acetic anhydride (3 c c.), diluted with 10 c.c. of water and extracted with ether to remove the unreduced nitro compound. The aqueous solution on neutralising with sodium carbonate furnished about 1 5 g. of 2 : 4-dimethyl-5-acetaminothiazole identified by comparing with the specimen prepared previously by the Curtius reaction.

The reduction could also be carried out by iron dust in acidified alcohol

2 : 4-*Dimethylthiazole.*—As a result of a number of experiments, the following has been found to be the best and most rapid method for the preparation of this compound in quantity. Acetamide (100 g.) and phosphorous pentasulphide (75 g) covered with a layer of benzene (100 c c) was gently warmed on the water-bath and to the melt chloracetone (35 c c) in benzene (35 c c) was added in the course of about 30 minutes. When the addition was over, the mixture was refluxed for 1 hour more, poured into ice and made acidic with hydrochloric acid. The solution was steam-distilled to remove benzene and unreacted chloracetone. 2 : 4-Dimethylthiazole was recovered by basifying the solution and steam-distilling; yield, 35–40 c.c.

2 : 4-*Dimethyl-5-bromothiazole.*—2 : 4-Dimethylthiazole (38 g.) in chloroform (100 c.c.) was treated with bromine (54 g.) in chloroform (50 c.c.) in the cold. The reaction mixture was allowed to stand at room temperature for one hour and the solvent removed. The orange red crystalline perbromide obtained was washed with ether (yield, 85–90 g.), suspended in

ice-water (150 g.), made alkaline, the heavy oil separated, dried over potash and the residue (50 g.) fractionated. The bromo compound distilled at 85–90°/10 mm. (yield, 45 g.). By passing dry hydrogen chloride into the ethereal solution of the bromo compound the hydrochloride was obtained (Found: Cl, 14·99; C₈H₇NSBrCl requires Cl, 15·52%).

The bromo compound did not react with urotropin, potassium phthalimide, or acetylsulphanilamide and copper powder. It did not form the Grignard reagent with magnesium under the usual conditions. By heating 11 g. of the bromo compound with zinc dust (15 g.) and acetic acid (50 c.c.) for 16 hours, the compound was debrominated and 2·4-dimethylthiazole was obtained in quantitative yield.

2-Hydroxy-4-methyl-5-(p-tolueneazo) thiazole (XI).—A solution of *p*-toluidine (5 g.) in water (40 c.c.) and concentrated hydrochloric acid (15 c.c.) was diazotised with a solution of sodium nitrite (4·4 g.) and the diazo solution poured into a cold solution of 2-hydroxy-4-methylthiazole (5·7) in sodium hydroxide (50 c c of about 4%). The bright yellow azo-compound that separated immediately was filtered off, washed with water and dried (yield, 9 5 g) On crystallising from benzene or acetic acid it was obtained in yellow needles which darkened at 180° and decomposed completely above 190° (Found: N, 17·62, C₁₁H₁₁N₃OS requires N, 18·0%).

2-Hydroxy-4-methyl-5-aminothiazole (XII).—The foregoing freshly prepared azo compound (9 5 g.) was dissolved in dilute sodium hydroxide (100 c.c. of 4%) and treated with sodium hydrosulphite (36 g.). After warming at 60° C. for 1 hour, the pale yellow solution was cooled and extracted with ether On acidifying the alkaline solution with 50% acetic acid a granular solid separated which was collected, washed with water and dried (yield, 5 g.) It crystallised from alcohol and had m p 153–55° (Found: N, 21·21; C₄H₆ON₂S requires N, 21·53%). It was not soluble in dilute mineral acids and on drying at 100° turned brownish With acetsulphanilyl chloride it yielded an acetsulphanilamido derivative thus establishing the presence of the amino group in the compound

8. SUMMARY

Synthesis of 5-aminothiazole derivatives has been investigated by various methods. Conditions have been worked out to convert the 5-carboxylic

ester into the 5-acetamino grouping. Accordingly, 4-methyl-5-acetamino-thiazole, 2 : 4-dimethyl-5-acetaminothiazole, 2-chloro-4-methyl-5-acetamino-thiazole, 2 : 5-diacetaminothiazole and 2 : 5-diacetamino-4-methylthiazole have been synthesised starting from the corresponding esters by the Curtius reaction. The reaction failed to yield the 5-acetamino compounds from ethyl thiazole-5-carboxylate and ethyl 2-bromothiazole-5-carboxylate. 2 : 4-Dimethyl-5-acetaminothiazole was hydrolysed to the amino compound while this was not successful in the case of 4-methyl-5-acetaminothiazole.

The oxime of 4-methyl-5-acetylthiazole on treatment with phosphorous pentachloride yielded by Beckman transformation 4-methyl-4-acetamino-thiazole while with acetic anhydride and hydrogen chloride the acetate of the oxime was obtained Similarly the oxime of 2 · 4-dimethyl-5-acetyl-thiazole with phosphorous pentachloride furnished in about 10% yields 2 : 4-dimethyl-5-acetaminothiazole and with acetic anhydride and hydrogen chloride the acetate of the oxime.

Nitration of 2-acetaminothiazole yielded a nitration product which is provisionally considered as 2-acetamino-5-nitrothiazole; hydrolysis of this yielded 2-amino-5-nitrothiazole which could be prepared directly also from 2-aminothiazole These two nitro compounds underwent reduction with all the usual reducing agents but the reduction products as such or after acetylation could not be isolated 2 4-Dimethyl-5-nitrothiazole could be reduced with iron to the amino compound which on acetylation yielded 2 : 4-dimethyl-5-acetaminothiazole.

2-Hydroxy-4-methylthiazole underwent coupling with diazotised *p*-toluidine to yield an azo dye which on reduction furnished 2-hydroxy-4-methyl-5-aminothiazole.

The bromine atom in 2 : 4-dimethyl-5-bromothiazole could not be converted into the amino or substituted amino groupings; the bromo compound did not form the Grignard reagent but was easily debrominated by zinc dust. 2 : 4-Dimethylthiazole did not react with hydrazoic acid to furnish 2 : 4-dimethyl-5-aminothiazole. Acetylglycineamide did not react with phosphorous pentasulphide to furnish 2-methyl-5-aminothiazole by the Gabriel's reaction.

REFERENCES

1.	Wallach, O	*Ber.*, 1874, **7**, 902
2.	Hellsing, G.	*Ibid.*, 1899, **32**, 1497 ; 1900, **33**, 1774 ; 1903, **36**, 3546.
3	Arnold and Scaife	*J. Chem. Soc.*, 1944, 103.
4	Weidel and Niemilowncz	*Monats.*, 1895, **16**, 742
5	Fischer and Ach	*Annalen*, 1895, **288**, 167.
6	Hromatka, O	*Ger Patent* 670,131 ; *C. A.*, 1939, **33**, 2909
7	Lindeman, H	*Helv Chim. Acta*, 1928, **11**, 1027
8	Barnum and Hamilton	*J Amer Chem. Soc.*, 1942, **64**, 540
9	Harrington and Moggridge	*J Chem. Soc.*, 1939, 443
10	Andersag and Westphal	*Ber.*, 1937, **70**, 2035
11	Smith and Sapiro	*Trans Royal Soc S Africa*, 1929, **18**, Pt 3, 229 ; *C A.*, 1930, **24**, 2130
12	Baumgarten, Dornow, Gutschmidt and Krehl	*Ber.*, 1942, **75**, 442 , *C A.*, 1943, 37, 3091
	Ganapathi and Venkataraman	*Proc Ind Acad Sci*, 1945, **22**, refer to Part III
13.	Ochiai, E	*J Pharm Soc Japan*, 1938, **58**, 1040 , *C A.*, 1939, **33**, 3791
14	Nagasawa, H	*Ibid.*, 1940, **60**, 271, 433 , *C A*, 1941, **35**, 458.
15	Wibaut and Jensen	*Rec trav chim*, 1934, **53**, 77 , *C A*, 1934, **28**, 4417
16	Robinson, R	*Outline of Electrochemical Theory of Organic Reactions*, 1932 (Institute of Chemistry, England)
17	Ochiai and Nagasawa	*Ber.*, 1939, **72**, 1470 . *C A*, 1939, **33**, 7782
18	Erlenmeyer, Bloch and Kiefer	*Helv chim Acta*, 1942, **25**, 1066
19	Bogert and Cherbcott	*Proc Nat Acad Sci*, 1924, **10**, 418 , A, 1925, **1**, 80 , *J Amer Chem Soc*, 1924, **46**, 2864
20.	Zerweck and Schubert	*Ger Patent* 729,853 , *C A.*, 1944, **38**, 382
21.	Huntress and Pfister	*J. Amer Chem Soc.*, 1943, **65**, 1667
22	Gabriel, S	*Ber.*, 1910, **43**, 134, 1283
	Gabriel and Bachster	*Ibid.*, 1914, **47**, 3170
	Bachster	*Ibid.*, 1914, **47**, 3163
	Miyamichi, E	*J Pharm Soc Japan*, 1926, No 528, 103 ; *C A.*, 1926, **20**, 2679
23.	Buchman and Richardson	*J. Amer Chem Soc*, 1939, **61**, 892
24	Hazlet and Dornfeld	*Ibid.*, 1944, **66**, 1781

CHEMISTRY OF THE THIAZOLES

Part II. Synthesis of 4-Aminothiazole Derivatives

By K. Ganapathi and (Mrs.) Alamela Venkataraman

(From the Department of Chemotherapy, Haffkine Institute, Parel, Bombay)

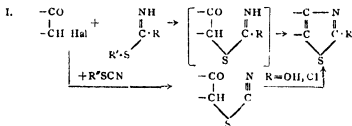In Part I of this series,[1] a number of methods for the synthesis of 5-amino-thiazole derivatives were described. This Part deals with the attempts made to synthesise 4-aminothiazole and derivatives.

By the action of dilute sulphuric acid on thiocyanoacetamide (I) Miolati[2] obtained a compound described as "isothiohydantoin" (II) the reaction proceeding as follows:
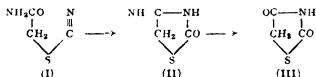
We have confirmed the preparation of this compound but our attempts to convert it into 4-acetaminothiazole or 2:4-diacetaminothiazole were unsuccessful. This compound is very feebly basic and could be extracted from dilute sulphuric acid solution with ether. It did not react with acetic anhydride to yield the acetyl derivative. It is very unstable to dilute acid or alkali. With dilute hydrochloric acid or sulphuric acid it is converted into 2 : 4-diketothiazolidine (III)

We next attempted to synthesise 4-aminothiazoles from the corresponding thiazole-4-carboxylic esters. Ethyl 2-methylthiazole-4-carboxylate prepared by the action of thioacetamide on bromopyruvic ester, could not be converted into 2-methyl-4-acetaminothiazole by the Curtius method. But ethyl 2-aminothiazole-4-carboxylate[3] was converted into 2:4-diacetamino-thiazole by the Curtius method.

While we were investigating the above method for the synthesis of 4-aminothiazoles, an abstract of a German Patent[4] came to our notice wherein the fusion of thiourea with chloracetonitrile is claimed to produce 2 : 4-diaminothiazole hydrochloride (IV), the reaction proceeding obviously as follows:

A2

$$\begin{array}{ccc}
\text{N}{=}\text{C} \quad \text{NH}_2 & \text{NH}{-}\text{C}{-}\text{N} & \text{NH}_2 \cdot \text{C}{-}\text{N} \\
| \quad + \quad | & | \quad \parallel & \parallel \quad \parallel \\
\text{CH}_2\text{Cl} \quad \text{CS}\cdot\text{NH}_2 & \text{CH}_2 \quad \text{C} \quad \text{NH}_2 \quad \text{or} & \text{CH}_2 \quad \text{C}\cdot\text{NH}_2 \\
& \diagdown\diagup & \diagdown\diagup \\
& \text{S} & \text{S} \\
& & \text{(IV)}
\end{array}$$
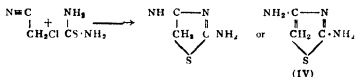
We have now found that this reaction proceeds with surprising ease in alcoholic solution to furnish in quantitative yields the hydrochloride of 2 : 4-diaminothiazole (IV). The free base could not be isolated and in this respect it resembles 4-aminoglyoxaline   On acetylation a diacetamino derivative was obtained which was found to be identical with 2 : 4-diaceta-minothiazole prepared from ethyl 2-aminothiazole-4-carboxylate as described above. This new reaction was further investigated using in the place of thiourea other representative thioamides; but these did not yield the required 4-aminothiazole derivatives. The 4-amino group in these cases appears to split off by hydrolysis   Thioformamide and thioacetamide when condensed individually with chloroacetonitrile produced about one molecular equivalent of ammonium chloride and an oil which has not so far been characterised. Ammonium thiocarbamate when treated similarly produced one molecular equivalent of ammonium chloride and in addition ammonia also evolved from the reaction mixture. Ethyl thio-oxamate (NH$_2$.CS. COOEt) condensed with chloroacetonitrile to yield a product, m p. 140, which appears to be 4-ketothioazoline-2-carboxylate   Full details of these results will be published shortly

<div align="center">EXPERIMENTAL</div>

Ethyl 2-methylthiazole-4-carboxylate.—Pyruvic ester (8 g.) was brominated with bromine (11 g.) in carbon disulphide (80 c.c.) according to Erlenmeyer.[8] After removing the hydrogen bromide with solid barium carbonate, the crude ester obtained was treated with thioacetamide (3 g.) in alcoholic solution and the product worked up as usual. The thiazole ester obtained (1 g.) crystallised in colourless elongated plates and had m.p. 64–65°. (Found N, 7·75; C$_7$H$_9$O$_2$NS requires N, 8·18%.)

2 : 4-*Diaminothiazole hydrochloride.*—Thiourea (8·9 g.) in hot alcohol (50 c.c. of 50%) was treated with chloroacetonitrile (8·9 g.). The clear solution was refluxed for 15 minutes when it set to a crystalline mass. It was cooled, filtered, washed with a little alcohol and dried. The first crop (14 g.) separated in bunches of thick rectangular plates. The mother liquor on evaporation to dryness yielded 3·9 g more of the product. On crystallisation from 75% alcohol the compound obtained turns brownish at 170° and does not melt below 275°. (Found: N, 27·52; Cl, 23·18; C$_3$H$_6$N$_3$SCl requires N, 27·72; Cl, 23·40%.) It yielded a picrate which, after

crystallisation from boiling water, darkens at 210° and melts with decomposition above 290°.

2 : 4-*Diacetaminothiazole.*—(i) The foregoing amino compound (2 g.) was refluxed with acetic anhydride (5 c.c.) and pyridine (5 c.c.) for 45 minutes, diluted with water and the solid that separated (2·4 g.) crystallised from boiling water. The diacetamino compound separated in thick rhombic plates melting at 239–41°. (Found: N, 20 99; $C_7H_8N_3O_2S$ requires N, 21·10%.)

(ii) Ethyl 2-aminothiazole-4-carboxylate (4 g.) in rectified spirits (10 c.c.) and hydrazine hydrate (3 c.c. of 84%) were refluxed for 6 hours. The residue obtained after distilling off the solvent was dissolved in boiling water (charcoal) and evaporated to dryness (yield of the hydrazide, 3·5 g.). On crystallisation from boiling water the hydrazide melted at 183–94°. The crude hydrazide (2 g.) in water (15 c.c.) and acetic acid (3 c.c.) was cooled to 0° and carefully treated with sodium nitrite (1 g.) in water (6 c.c.). The azide which precipitated as a brown solid was washed with ice-water and dried (yield 1 8 g.). The crude azide was decomposed by warming with a mixture of acetic anhydride (3 c.c.) and acetic acid (5 c.c.). On working up as usual, 2 · 4-diacetaminothiazole was obtained which crystallised in white shining plates and had m.p. 234–36°. This did not depress the melting point of the previously described sample on admixture.

We thank Lt.-Col. S. S. Sokhey, Director, for his kind interest in these investigations and the Lady Tata Memorial Trust for the award of a scholarship to one of us (A.V.).

SUMMARY

That chloracetonitrile condenses with thiourea to yield 2:4-diaminothiazole hydrochloride has been confirmed. The diacetamino compound prepared from this by acetylation has been found to be identical with that prepared from ethyl 2-aminothiazole-4-carboxylate by the Curtius method. Chloracetonitrile reacted with other thioamide compounds but the products are found to be not 4-aminothiazole derivatives.

Ethyl 2-methylthiazole-4-carboxylate could not be converted into 2-methyl-acetaminothiazole.

REFERENCES

1. Ganapathi and Venkataraman *Proc Ind. Acad. Sci.,* 1945, **22A**, 343
2. Miolati, A. *Gazetta,* 1893, **23**, 1, 90
3. Erlenmeyer and Morel *Helv. chim. Acta,* 1942, **25**, 1073.
4. Zerweck and Schubert *Ger. Patent,* 729, 853; *C. A.,* 1944, **38**, 382.
5. Hunter and Nelson *Canad. J. Res.,* 1941, **19 B**, 296; *Brit. Chem. Abs.,* 1942, A 2, 116.

CHEMISTRY OF THE THIAZOLES

Part III. Synthesis of Thiazole Derivatives Unsubstituted in Position 2 : An Evaluation of Various Possible Methods

By K. GANAPATHI AND (MRS.) ALAMELA VENKATARAMAN

(From the Department of Chemotherapy, Haffkine Institute, Parel, Bombay)

INTRODUCTION

A NUMBER of thiazole derivatives unsubstituted in position 2 of the thiazole ring were required in connection with some other work and we are also interested in the manufacture of 4-methyl-5-β-hydroxyethylthiazole which is required as an intermediate in the synthesis of thuamine chloride. Though a number of methods have been mentioned in literature, most of them are covered up in patents, the abstracts of which available do not disclose details adequate enough for reproducing the results claimed. We, therefore, undertook to study and compare all possible methods of synthesis of these compounds. The results obtained and the conclusions drawn so far are presented in this paper. An account of the various efforts made to prepare 4-methyl-5-β-hydroxyethylthiazole will appear in a separate communication.

For the synthesis of the thiazole compounds, several methods are available which can be classified into the following two groups:

I.

$$\begin{array}{c} -CO \\ | \\ -CH \ Hal \end{array} + \begin{array}{c} NH \\ \| \\ C \cdot R \end{array} \nearrow R'\cdot S \longrightarrow \left[\begin{array}{cc} -CO & NH \\ | & \| \\ -CH & C \cdot R \\ & S \end{array} \right] \longrightarrow \begin{array}{cc} -C & N \\ \| & \| \\ -C & C \cdot R \\ & S \end{array}$$

$$+ R''SCN \longrightarrow \begin{array}{cc} -CO & N \\ | & \| \\ -CH & C \\ & S \end{array} \quad R = OH, Cl$$

where R = H, R = H, Me, COOEt,¹ NH₂, OMe, OEt.
R - NH₄, R=OH, SH³.
R''=Na, K, Ba, NH₄.

II.

$$\begin{array}{cc} -CH-NH \\ | \ | \\ R'' \ CO \ CO\cdot R \end{array} \xrightarrow{P_2S_5} \begin{array}{cc} -C-N \\ \| \ \| \\ R''\cdot C \ C\cdot R \\ S \end{array}$$
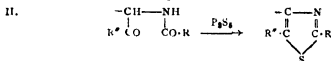
where R and R'' are alkyl, aryl, or aralkyl groups.⁵

362

In both these methods, the reactions that are of interest to us at present are those in which R is hydrogen or where it is otherwise, it should be capable of subsequent conversion into hydrogen. Thus, seven methods are theoretically possible of which three are examined here. The preparation of 2-mercaptothiazole derivatives[2] and their oxidation to the thiazoles[3] have been previously investigated in some cases by others.

METHOD 1

The only method which yields directly the 2 unsubstituted thiazole derivative involves the condensation of the α-chloroketone or aldehyde with thioformamide. This method has been employed fairly frequently to synthesise a number of thiazoles. Though *prima facie* this appears to be the best method, the drawbacks are that the yield in the preparation of thioformamide, especially on a large scale, is unsatisfactory, it is not very stable, particularly under acidic conditions, and the yields in the condensations are not uniformly good. The condensation of the α-chloroketone with a mixture of formamide and phosphorus pentasulphide without the isolation of thioformamide[4] was tried in a variety of solvents and of these only ether gave satisfactory results. In the case of the α-chloroketones which are stable, the treatment of the mixture without any solvent yielded the best results; the total time taken for the reaction was very much shortened and the isolation of the thiazole derivative formed presented no difficulties. Thus, four representative compounds have been prepared by this method. By reacting a mixture of phosphorous pentasulphide, formamide and ethyl α-chloroacetoacetate, ethyl 4-methylthiazole-5-carboxylate has been prepared in quantity; this method appears to be the best so far worked out for the large-scale preparation of this compound. Similarly, 4-methylthiazole, 4:5-dimethylthiazole and 4-methyl-5-acetylthiazole have been prepared in good yields and these methods replace the older ones described in literature for their preparation in quantity. We find that this method can be used in other cases also wherein the chloroketone is fairly stable under the experimental conditions. But the parent compound thiazole could not be prepared by treating chloroacetal with a mixture of formamide and phosphorous pentasulphide; so also, ethyl thiazole-4-carboxylate was not obtained from bromopyruvic ester.

METHOD 2

Of all the methods described for the synthesis of the thiazole compounds, the one which is easily the best involves the condensation of thiourea with α-halogenoketones or aldehydes to yield the corresponding 2-aminothiazoles. Thiourea is a very cheap material, the condensation could be carried out

even in distinctly acidic media, an advantage not shared by other methods, and the yields are comparatively very good. The conversion of the 2-amino-thiazole derivatives into those unsubstituted in position 2 was tried by the two methods available involving the Sandmeyer's reaction, viz., the conversion of the amino group into the halogen atom which is subsequently reduced to the hydrogen atom and the direct replacement of the diazonium group by the hydrogen atom.

The conversion of the halogen atom into hydrogen either by means of zinc dust in acetic acid or catalytically with palladium, proceeds in very good yields But the preparation of the 2-halogenothiazoles as reported in literature was far from satisfactory The diazotisation of 2-aminothia-zole and some derivatives has been reported,[6] but we could not repeat these experiments even in moderate yields. McLean and Muir[7] have also recently recorded their inability to repeat many of the experiments of the earlier investigators; these authors after many trials could prepare 2-chlorothia-zole in not more than about 20 per cent. yields by diazotising 2-aminothia-zole in hydrochloric acid and treating the diazonium solution with cuprous chloride. Erlenmeyer and Morel[8] have recently converted ethyl 2-amino-thiazole-4-carboxylate into ethyl 2-bromothiazole-4-carboxylate in about 70 per cent. yields by diazotising the aminothiazole derivative in a mixture of phosphoric acid and nitric acid and treating the diazonium solution with a large excess of hydrobromic acid and copper powder. Since it is impera-tive that the amine should be in the ammonium form to undergo diazotisa-tion,[9] we tried the condition for the diazotisation of the weakly basic amines with notable success. The diazotisation of 2-aminothiazole by the addi-tion of the amine dissolved in acetic acid to nitrosyl sulphuric acid did not proceed on in as good yields as when the amine was dissolved in sulphuric acid and added to nitrosyl sulphuric acid.[11] In a mixture of phosphoric acid (70 to 85 per cent) and concentrated nitric acid, the diazotisation pro-ceeded on well as also the 'inverted diazotisation ' of Walker and Hodgson[10] using sulphuric acid and glacial acetic acid. Morgan and Morrow[11] have diazotised 2-aminothiazole both in perchloric acid and dilute sulphuric acid (20 per cent.). We have found that the best yields are obtained by using about 40 to 50 per cent. sulphuric acid The results of trying various conditions are presented in Table I

The decomposition of the diazonium salt was carefully investigated and herein a good improvement was effected. Heating the diazonium solu-tion with concentrated hydrochloric acid[8] gave only traces of the chloro-thiazole; with concentrated hydrochloric acid and copper powder the yield was 20 per cent.; cuprous chloride increased the yield to about 34 per cent.

and the best yield of 70 per cent. was obtained when a mixture of copper sulphate and sodium chloride was used in aqueous medium.[11] While we were trying the effects of various metallic chlorides in the place of sodium chloride, the paper of Hodgson, Birtell and Walker[12] came to our notice. These authors have found that ferric chloride gives good results but is not superior to sodium chloride. By using a mixture of sodium bromide and copper sulphate for the decomposition of the diazo solution 2-bromothiazole is obtained in good yields. The advantage in this method is that only one molecular equivalent of sodium bromide is used while Erlenmeyer and Morel[8] use a large excess of hydrobromic acid. It is worthwhile mentioning here that 2-halogenothiazole is an intermediate in the manufacture of the drug sulphathiazole according to a patented process and the only factor that prevented the commercial exploitation of this method was the bad yield in which the 2-halogenothiazoles were obtained till now.

A number of 2-aminothiazole derivatives were subjected to the reaction to study the effects of the various substituents on the ease of diazotisation and decomposition of the diazonium salts. As expected, the various substituents in the positions 4 and/or 5 of the thiazole ring in the 2-aminothiazole derivatives showed some significant and striking effects in the above reactions. Thus 2-chloro-5-methylthiazole could be prepared in about 76 per cent. yields and 2-chloro-5-ethylthiazole in 70 per cent. yields from the corresponding 2-aminothiazole derivatives.[27] The diazotisation of the higher homologues did not proceed on well because the basicity of these products decreased very much and no stable ammonium salt could be obtained. As a striking contrast to the case of 2-amino-5-methylthiazole, the 4-methyl isomer yielded 2-chloro-4-methylthiazole in poor yields. 2-Amino-4:5-dimethylthiazole yielded the corresponding 2-chloroderivative in about 50 per cent. yields. Ethyl 2-aminothiazole-5-carboxylate furnished the 2-chloro derivative in very poor yields but the 2-bromo compound could be prepared in about 60 per cent. yields under a set of conditions. In the case of 2-amino-4-methylthiazole-5-carboxylate the chloroderivative was obtained in about 45 per cent. yields, a red dye accompanying this product. 2-Amino-4-carbethoxymethylthiazole and 2-amino-4-methyl-5-carbethoxy-methylthiazole could not be smoothly diazotised, the diazonium salt rapidly undergoing decomposition. 2-Amino-5-nitrothiazole[28] could not be diazotised smoothly without spontaneous decomposition and formation of highly coloured products under all conditions. However, the 2-chloro-and 2-bromo-compounds required by us for many purposes, was prepared in good yields by diazotising 2-amino-5-nitrothiazole in sulphuric acid in the presence of sodium halide and copper sulphate. This new modification

was tried in a number of cases in this Laboratory and as a result of the experiments we conclude that to obtain good yields by this method it is necessary that the diazotisation of the amine should proceed on very fast and the diazonium salt should also decompose very rapidly. When tried in the case of 2-aminothiazole and 2-aminothiazole-5-carboxylate this modified method gives lower yields than the usual method. The results presented above indicate that the preparation of the 2-halogenothiazoles from the 2-aminothiazole derivatives is not of universal applicability.

The conversion of 2-aminothiazole into thiazole by the Sandmeyer's reaction according to Popp[14] is not at all satisfactory.[7] 2-Aminothiazole was diazotised with sodium nitrite solution in a mixture of phosphoric acid and nitric acid or 40 per cent. sulphuric acid and the diazonium solution was treated with (a) methyl alcohol containing a suspension of copper suboxide,[15] (b) methyl alcohol containing a suspension of copper bronze, (c) an aqueous suspension of calcium hypophosphite[15,17] and (d) alkaline formaldehyde.[18] The yields of thiazole in the four experiments were respectively 32 per cent., 28 per cent., 36 per cent., and traces. The use of hypophosphorus acid in the place of calcium hypophosphite gave slightly lower yields. By using the method of Hodgson,[15] diazotisation (inverted) with nitrosylsulphuric acid in sulphuric acid and treating the diazo product with cuprous oxide in methyl alcohol, thiazole was obtained in 30 per cent. yields. The reduction with calcium hypophosphite is the best and most convenient method for the actual working. Starting from 2-amino-5-methylthiazole, 5-methylthiazole was obtained in 60 per cent yield by using calcium hypophosphite and in 40 per cent yield by using cuprous oxide in methyl alcohol. 5-Ethylthiazole could similarly be obtained in 56 per cent. yield. The other 2-aminothiazole derivatives gave very unsatisfactory yields with these reagents. Thus the direct conversion of the 2-amino group into the hydrogen is advantageous only to prepare 5-methyl and 5-ethylthiazoles. In the other cases it is advantageous to prepare the 2-chloro or 2-bromo compounds and then reduce them.

METHOD 3

The third method of preparing thiazole derivatives unsubstituted in position 2 consists in synthesising 2-hydroxythiazole derivatives and then converting the hydroxyl group into the hydrogen atom. The method of replacing the hydroxyl by hydrogen by distilling with zinc dust[19] proceeds in bad yield and therefore it is preferable to convert the hydroxyl group into the chlorine atom and then reduce it to hydrogen. There are two methods available for the synthesis of the 2-hydroxythiazole derivatives from the α-halogenoketones. The first is the conversion of the α-halogenoketone

into α-thiocyanoketone by treatment with ammonium, potassium or bette barium thiocyanate and then isomerising the thiocyanoketone. This method has been employed by Andersag and Westphal[20] for the synthesis of 4-methy 5-β-hydroxyethylthiazole but they have not stated the yields obtained in the various stages. The other less known method is due to Marchesini[21] which consists in the condensation of the α-halogenoketone with ammonium thiocarbonate as follows:

$$\begin{array}{c} -CO \\ | \\ -CH \cdot Cl \end{array} + \begin{array}{c} NH_2 \\ | \\ CO \\ Am \cdot S \end{array} \longrightarrow \left[\begin{array}{cc} -CO & NH_2 \\ | & | \\ -CH & CO \\ S \end{array} \right] \longrightarrow \begin{array}{cc} -C\!-\!N \\ \| & \| \\ -C & C\cdot OH \\ S \end{array}$$
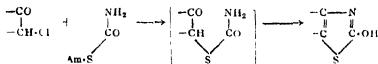
These methods have not been studied in detail.

Our attempts to prepare the hitherto unknown parent compound 2-hydroxythiazole, required by us for more than one purpose, by condensing dichlorether or chloroacetal with the thiocyanates or ammonium thiocarbamate were unsuccessful. The condensation of chloroacetone with the thiocyanates as also with ammonium thiocarbamate to yield 2-hydroxy-4-methylthiazole has previously been studied by Hantzsch[22] and by Tcherniac.[23,2] After comparing these two methods we find that the condensation of chlor acetone with ammonium thiocarbamate furnishes 2-hydroxy-4-methylthiazole in distinctly better yields (90 per cent.). Though thiocyanoacetone could be obtained in good yields the isomerisation could not be effected quantitatively, tarry and resinous products being also produced, the nature of which has not been investigated. The reaction of α-chloromethylethylketone with ammonium thiocarbamate led to the production of 2-hydroxy-4:5-dimethyl thiazole in about 25 per cent. yields, there being formed an oily side product. By treating the chloroketone with barium thiocyanate, the thiocyano compound could be obtained in good yields; on isomerising this with hydrochloric acid the hydroxythiazole derivative was obtained in about 20 per cent yields, while with concentrated sulphuric acid in glacial acetic acid the yield increased to 40 per cent., an oily by-product being produced in both cases. *Sym.* Dichloroacetone condensed with two molecular equivalents of ammonium thiocyanate or potassium thiocyanate to furnish in good yields 2-hydroxy-4-thiocyanomethylthiazole (III); ammonium thiocarbamate, on the other hand, furnished in about 25 per cent. yields

$$\begin{array}{cc} NCS\cdot CH_2\cdot C\!-\!\!-\!N & Cl\cdot CH_2\cdot C\!-\!\!-\!N \\ \| & \| & \| & \| \\ HC & C\cdot OH & HC & C\cdot OH \\ S & S \\ (III) & (IV) \end{array}$$
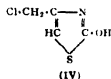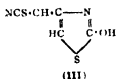
2-hydroxy-4-chloromethylthiazole (IV), along with a by-product which could not be purified. When ethyl α-chloroacetoacetate was treated with ammonium thiocyanate or potassium thiocyanate, a product, m.p. 128°, was obtained in poor yields; treatment of ethyl α-thiocyanoacetoacetate with acids also yielded the same product. This compound is described in literature[38] as ethyl 2-hydroxy-4-methylthiazole-5-carboxylate. On the other hand, treatment of ethyl α-chloroacetoacetate with ammonium thiocarbamate furnished in very good yields a product, m p 175°, whose properties agree with that of structure ethyl 2-hydroxy-4-methylthiazole-5-carboxylate We first surmised that these two compounds might be dimeric just like the " α- and β-rhodim " of Tcherniac.[2,3] But on treatment with phosphorous oxychloride, the product, m p 175°, yielded ethyl 2-chloro-4-methylthiazole-5-carboxylate while the lower melting product did not yield this chloro compound. Thus while we are sure that the higher melting product (m.p. 175°) is ethyl 2-hydroxy-4-methylthiazole-5-carboxylate, the structure assigned to the lower melting product appears to be doubtful In the case of chloroacetylacetone a similar result was obtained. On treating this with ammonium thiocarbamate a crystalline product (m.p. 210-12°) was obtained in good yields and it is identical with 2-hydroxy-4-methyl-5-acetylthiazole obtained by Nagasawa[31] from 2-hydroxy-4-methylthiazole by acetylation and also by the action of acetylchloride and aluminium chloride The action of barium thiocyanate on chloroacetylacetone furnished not the abovementioned product but one of m.p 228°, the structure of which we have not fixed up Thus we find that the chloro derivatives of the β-ketonic ester or β-diketone do not yield the same product on treatment with ammonium-thiocarbamate and with barium or any alkali metal thiocyanate. While the product obtained with ammoniumthiocarbamate has been definitely established here to be the expected 2-hydroxythiazole derivative, that obtained with the thiocyanates is of doubtful structure

In the condensation of thiourea with α-halogenoketones or aldehydes, the 2-aminothiazole derivatives are formed usually in good yields with no by-products But in the isomerisation of the α-thiocyanoketones or in the condensation of ammonium thiocarbamate with α-chloroketones, in addition to the hydroxythiazole derivatives (which themselves in many cases are formed in poor yields) other products are also formed, the nature of which has not been investigated so far. The reason appears to be that in the case of thiourea, because of the symmetry in structure of the reagent, there is only one way in which the reaction can proceed on. But in the other cases the reaction can take at least two courses as follows.

```
 -CO            -CO    N     ⎡-C·OH  N ⎤     -C——N
  |    + R·SCN —— |    ‖‖‖ →  ‖  ‖‖ →     ‖‖
 -CH·Cl         -CH    C     ⎣-C    C  ⎦     -C  C·OH
                     \/              \/              \/
                     S               S               S
                                                    (V)

              CO           ⎡-C·OH      ⎤    -C——O
               |    →       ‖           →    ‖  ‖
             ·CH  C≡N       -C   C≡N         -C  C·NH
                  \/           \/              \/
                  S            S               S
                                             (VI)

 -CO                        -CO
  |   + NH₂·S·CO·NH₂ ——   CH    CO·NH₂  ——   (V) or (VI)
 -CH·Cl                      \/
                             S
```
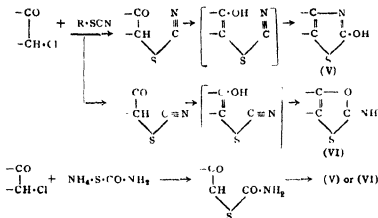
There are grounds to suggest that in many of the reactions, compounds of structure (VI) might also be produced in addition to the 2-hydroxythiazole derivatives.

Phosphorous oxychloride appears to be a reliable reagent for the conversion of the 2-hydroxythiazole into 2-chlorothiazole derivatives. We have found that 2-hydroxy-4:5-dimethylthiazole and ethyl 2-hydroxy-4-methylthiazole-5-carboxylate (m.p 175°) give the corresponding 2-chlorothiazole derivatives in theoretical yields on treatment with phosphorous oxychloride.

Another possible and cheap method of preparing the 2-chlorothiazole derivatives is to treat the α-thiocyanoketone derivatives with dry hydrogen chloride. By this method Tcherniac[24] has obtained a mixture of 2-hydroxy-4-methylthiazole and 2-chloro-4-methylthiazole from thiocyanoacetone The thiocyanoketone obtained from α-chloromethylethylketone on saturation with dry hydrogen chloride furnished in good yields 2-chloro-4:5-dimethyl-thiazole; no hydroxy compound was formed in this case. Also, the action of phosphorous oxychloride on the thiocyano compound yielded the same chloro compound along with a small amount of a crystalline product. The thiocyano compound prepared from α-chloroacetoacetate when treated with dry hydrogen chloride yielded an oil which on allowing to stand for many weeks deposited crystals of the chloro compound.

<div align="center">EXPERIMENTAL</div>

Ethyl 4-methylthiazole-5-carboxylate.—This has been prepared by many workers[39] by the action of thioformamide on α-chloro (or bromo) aceto-acetate. After many trials, varying the quantities of the reactants, the following method has been found to be the best

A mixture of phosphorous pentasulphide (13·2 g.), formamide (13·5 g.) and ethyl α-chloroacetoacetate (33 g.) was allowed to react, first cooled in ice-water, then at room temperature and finally by heating under reflux. The mixture was diluted with water, acidified with hydrochloric acid, extracted with ether, the acid product made just basic and steam-distilled (or extracted with ether). The thiazole ester obtained passed over at 230–36° (most of it at 233°); yield, 26 c.c.

4-Methylthiazole.—McLean and Muir[7] who required this compound in quantity have prepared it by reducing 2-chloro-4-methylthiazole in turn obtained from thiocyanoacetone according to Tcherniac.[34] This is very conveniently prepared by reacting monochloracetone (18·5 g.), formamide (13·5 g.) and phosphorous pentasulphide (13·2 g.) and working up as described in the previous preparation. One thus obtains 6–7 c.c. of 4-methylthiazole.

4:5-Dimethylthiazole.—This compound has been prepared by Buchman, Reims and Sargent[5] by the oxidation of 2-mercapto-4:5-dimethylthiazole By reacting α-chloromethylethylketone (21 g.) with a mixture of formamide (13·5 g.) and finely powdered phosphorous pentasulphide (13·2 g.) and working up as usual, 11·5 g. of 4:5-dimethylthiazole was obtained, b.p. 158°; picrate m.p. 186–87°. Buchman, *et al.*[5] record b.p. 81–83°/59 mm for 4:5-dimethylthiazole and m.p. 186–87° for its picrate.

4-Methyl-5-acetylthiazole.—The preparation of this compound has very recently been reported by Baumgarten, *et al.*[30] by the action of thio-formamide on chloracetylacetone and also from ethyl 4-methylthiazole-5-carboxylate by a more involved process and in lower yields. Treating a mixture of formamide (20 g.) and phosphorous pentasulphide (12 g.) with chloroacetylacetone (13·5 g.) and working up as usual, 9·5 g. of 4-methyl-5-acetylthiazole was obtained, b. p. 226°; picrate, m.p. 106–07. Baumgarten, *et al.* record b.p. 107–08°/13 mm. for 4-methyl-5-acetylthiazole and m.p. 108° for the picrate. The ketone is water-soluble and could not be steam-distilled.

2-Chlorothiazole.—A typical experiment is as follows:—2-Amino-thiazole (30 g. of the distilled product) was dissolved in phosphoric acid (120 c.c. of 80 per cent), the solution cooled to 5° C. and then concentrated nitric acid (60 c.c.) was slowly run in and stirred well. When the temperature of the mixture was 0° to − 5° C. it was diazotised with a solution of sodium nitrite (24 g.) the solution being allowed to flow under the surface of the liquid through a drawn out pipette or separating funnel. After all the nitrite was added, stirring was continued for 30 minutes more and then the diazonium solution was added to a solution of copper sulphate (50 g.) and

sodium chloride (50 g.) in 200 c.c. water kept cooled in ice-water. The evolution of nitrogen was immediate and ceased in about 10 minutes. The mixture was allowed to stand at the room temperature for about 30 minutes more, the acid partly neutralised and steam-distilled; the chlorothiazole rapidly passed over in the distillate. The results obtained in the various experiments under different conditions are given in Table I

TABLE I

Exp. No	Amino-thiazole taken	Medium of diazotisation	Sodium nitrite added	Agent used for decomposition	% Yield of chloro-thiazole
1	10 g.	HCl	7·5 g.	CuCl	20[a]
2	,,	H_3PO_4, 50 c.c., HNO_3, 20 c.c.	,,	Con. HCl	5–10[b]
3	,,	,, ,,	,,	Cu, 8 g ; HCl,	34
4	,,	,, ,,	,,	CuCl, 15 g ; HCl, 75 c.c.	34
5	30 g	H_3PO_4, 120 c.c., HNO_3, 60 c.c	24 g.	$CuSO_4$, 50 g.; NaCl, 50 g.	70[c]
6	,,	,,	,,	$CuSO_4$, 25 g ; NaCl, 50 g.	50
7	,,	,,	,,	$CuSO_4$, 100 g ; NaCl 100 g.	70
8	24 g.	AcOH, 75 c.c	18 g. in H_2SO_4 90 c.c	CuCl, 20 g ; HCl, 80 c.c	18[c]
9	10 g.	H_2SO_4, 20 c.c.	7·5 g in H_2SO_4 38 c.c.	$CuSO_4$, 16 g ; NaCl, 16 g	42[d]
10	,,	H_2SO_4, 16 c.c , H_2O, 60 c.c	7·0 g.	$CuSO_4$, 20 g.; NaCl, 18 g	35
11	,,	H_2SO_4, 16 c.c , H_2O, 30 c.c	,,	,, ,,	50
12	,,	H_2SO_4, 50 c.c. (1 1) $CuSO_4$, 25 g, NaCl, 11·7 g , H_2O, 50 c.c	8 4 g	Nil	30

[a] Condition of McLean and Muir.[7]

[b] Decomposition according to Schatzmann.[8]

[c] The amine is diazotised with nitrosylsulphuric acid

[d] Inverted diazotisation; after the amine was added to nitrosylsulphuric acid, glacial acetic acid (75 c.c.) was added below 5° C.

[e] In a number of experiments, along with 2-chlorothiazole, a small quantity of a crystalline solid, m.p. 70°-71°, also passed over; this slowly dissolved in alkali and the quantity obtained was not enough for further examination.

2-Chloro-5-nitrothiazole.

—A mixture of 2-amino-5-nitrothiazole[2a] (2·9 g.) in dilute sulphuric acid (20 c.c. of 1:1), copper sulphate (10 g.) and sodium chloride (4·7 g.) in water (25 c.c.) was cooled to 10° C. and treated carefully with sodium nitrite (1·55 g.) in water (5 c.c.) with rapid stirring. The evolution of nitrogen was steady and was complete in about 10 to 15 minutes. The chloro compound which had separated as a crystalline white solid was extracted with ether and purified by steam-distillation (yield, 1·5 g.). It crystallised from ether in hexagonal plates, m.p. 61°. (Found: N, 16·76; $C_3HO_2N_3SCl$ requires N, 17·02 per cent.)

2-Bromo-5-nitrothiazole.

—(i) This was prepared as above by treating a mixture of 2-amino-5-nitrothiazole (7·25 g.) in dilute sulphuric acid

(25 c.c. con. acid + 50 c.c water), copper sulphate (25 g.) and sodium bromide (10·3 g.) and sodium nitrite (4 g.) in water (10 c.c.). The yield of crude 2-bromo-5-nitrothiazole was 8·5 to 10·5 g. which on steam—distillation yielded a purer product (8–10 g.). On crystallisation from alcohol, ether or benzene, it separated in thick colourless plates, m.p. 91–92°. (Found: N, 13·47; $C_3HO_2N_2SBr$ requires N, 13·41 per cent.)

(ii) The same bromo compound could be prepared very easily directly from 2-aminothiazole as follows:

2-Aminothiazole (10 g.) was dissolved in concentrated sulphuric acid (30 c c.) below 15° C Fuming nitric acid (5 c.c.) (or a mixture of con. nitric acid, 10 c.c. and sulphuric acid, 10 c.c.) was then added with stirring at 10° C. Cooling then was discontinued when the temperature of the reaction mixture rose to 45° C. After allowing it to stand overnight at 30° the mixture was poured into a cold solution of copper sulphate (37·5 g.) and sodium bromide (31·8 g.) in water (125 c.c.) at 15° This m xture was diazotised as above described with sodium nitrite (8·4 g.) The crude 2-bromo-5-nitrothiazole obtained weighed 14·5 g. which on steam-distillation yielded 13 g. of the pure product in colourless crystals

TABLE II

4-and/or 5-Substituted 2-Halogenothiazoles

Exp. No.	2 Halogenothiazole prepared	Medium of diazotisation	b.p.	% Yield	N. percentage	
					Found	Required
1	2-Bromo	$H_3PO_4 + HNO_3$	171–74°	75	..	..
2	2-Chloro 5-methyl	,,	174–76°	65	..	..
3	,, ,,	H_2SO_4	,,	76	..	..
4	,, ,,	,,	,,	60ᵃ	..	..
5	2-Bromo-5-methyl	,,	192–200°	70	8·30	7·87
6	2-Chloro-5-ethyl	,,	192–93°	70	9·39	9·47
7	2-Bromo-5-ethyl-	,,	215°	50	6·88	7·30
8	2 Chloro-4 5 dimethyl	,,	190–92°	50	9·57	9·47
9	2-Chloro-4-methyl	,,	..	(Trace	..	..
10	2 Chloro-4-methyl-5-carbethoxy-	,,	M p. 50–51°	40	..	..
11	2-bromo 5-carbethoxy	,,	192– 94/5 mm.	60ᵇ	6·09	5·93

The diazotisation was carried out in a mixture of phosphoric acid and nitric acid as given in Table I in dilute sulphuric acid. The decomposition of the diazonium solution was effected by using about 1 2 molecular equivalents each of copper sulphate and sodium halide at about 0° C.

ᵃ In this case the diazonium solution was treated with cuprous chloride (15 g) and con. hydrochloric acid (60 c c.)

ᵇ This yield is obtained only if the diazotisation is carried out very rapidly and the solution added to the copper salt immediately. The chloro compound is formed in poor yields.

Preparation of thiazole and alkylthiazoles.—The 2-aminothiazoles were diazotised in a mixture of phosphoric acid and nitric acid or dilute sulphuric acid and the diazonium solution treated with the reagents mentioned. After the evolution of nitrogen ceased, the solutions were allowed to stand at the room temperature for about one hour and then steam-distilled after making them alkaline Steam-distillation was continued till the distillate did not yield any perceptible amount of picrate with a solution of picric acid. The distillate was acidified with concentrated hydrochloric (sufficient to fix all the basic material) and the solution concentrated to a small bulk. The solution was saturated with soda and extracted with ether repeatedly. From this extract the thiazole derivative was recovered 5-Ethylthiazole is very sparingly soluble in water and so can be separated from the distillate as such. Some of the typical experiments carried out are given in Table III.

TABLE III

Expt. No.	Thiazole prepared	Amine taken	Medium of diazotisn	Diazonium solution treated with	Percent-age yield
1	Thiazole	10 g	H₃PO₄ + HNO₃	Cu₂O 20 g MeOH, 200 c c	34
2	,,	,,	,,	Cu 20 g. MeOH, 200 c c	30
3	,,	,,	H₂SO₄, AcOH	Cu₂O, 20 g MeOH, 200 c c	28ᵃ
4	,,	,,	H₃PO₄ + HNO₃	CaHP, 40 g. Water, 120 c c	36
5	,,	,,	H₃SO₄	,,	30
6	,,	,,	,,	Formalin, 30 c.c. NaOH, 50 g.; H₂O, 250 c.c.)	5
7	5-Methylthiazole	11 5 g	,,	CaHP, 33 g. Water 120 c c	60
8	,, ,,	,,	,,	Cu₂O, 15 g MeOH, 150 c c	40
9	5-Ethylthiazole	6·2 g.	,,	CaHP, 25 g. Water, 80 c c	56ᵇ
10	,, ,,	,,	,,	HP Acid, 80 c c (33 %)	42
11	4-Methylthiazole-5 carboxylate	9·3 g	,,	CaHP, 30 g	16
12	,, ,,	,,	,,	Cu₂O, 30 g	15

CaHP · Calcium hypophosphite , HP Acid   Hypophosphorus acid
ᵃ Condition of Hodgson and Turner.¹ᵇ
ᵇ Found · N, 12·03 , C₆H₇NS requires N, 12·38%

Ammonium thiocarbamate —The preparation of this compound has been briefly mentioned by Tcherniac[4] but not described in detail. As a result of a number of experiments, the following was found to be the best method:

A cold saturated solution of ammonium thiocyanate (40 g. in 30 c.c. water) was gradually added to dilute sulphuric acid (290 c.c. of concentrated

acid diluted with 400 c.c. water) at about 25 ° C. and the liberated carbonyl sulphide passed into a saturated solution of alcoholic ammonia (250 c.c.) maintained at about 10°. The white crystalline solid that separated during 2 to 3 hours was filtered, pressed well, washed with ether and used directly. Yield, 20–25 g.

2-Hydroxy-4 : 5-dimethylthiazole.—(i) Ammonium thiocarbamate (13 g.) in water (15 c.c.) was gradually treated with α-chloromethylethylketone (10 g.) under cooling. On allowing the solution to stand overnight, some crystals and a colourless oil separated. The crystalline product was filtered and washed free from the adhering oil; yield, 1 g.; m.p. 146°. The oily product on extraction with alkali furnished a little more of the crystalline product. On crystallisation from benzene, alcohol or ligroin it separated in big rhombic plates or prisms; m.p. 147°   (Found: N, 11·25; C₅H₇ONS requires N, 10·85 per cent.)

(ii) α-Chloromethylethylketone (21 g.) in alcohol (15 c.c.) was treated with barium thiocyanate (33 g.). The mixture was shaken at intervals and allowed to stand overnight. The mixture was diluted with water and the turbid solution extracted with ether (5 × 20 c.c.). The ether extract yielded the thiocyanoketone as an oil (24 g.) The oil was boiled with concentrated sulphuric acid (2·5 c.c.) in glacial acetic acid (25 c.c.). The resulting dark solution was poured into water (150 c.c.), the pinkish crystals obtained were filtered, washed with water and dried (yield, 9·2 g. or 40 per cent. of theory); m.p. 146°. The mother-liquor on extraction with ether furnished 13·2 g. of the oily product which on allowing to stand for a number of weeks, furnished some more of the crystalline product.

On treating the thiocyanoketone obtained as above described with dilute hydrochloric acid (120 c.c. of 2 N) instead of a mixture of sulphuric acid and glacial acetic acid, only 4·8 g. (or 20 per cent.) of the hydroxy compound was obtained.

Ethyl   2-hydroxy-4-methylthiazole-5-carboxylate.—Ammonium thiocarbamate (13 g.) dissolved in water (10 c.c.) was gradually treated with ethyl α-chloroacetoacetate (18 c.c. 21·5 g.) adding pieces of ice to the mixture, which was then allowed to stand overnight. The crystalline product that had separated was filtered, washed with ice-water free from the adhering oily product (yield, 13 g.) This on crystallisation from boiling alcohol separated in glistening plates; m.p. 175°.   (Found: N, 7·50, 7·82; C₇H₉O₃NS requires N, 7·48 per cent.) This compound is soluble in dilute ammonia, alkali and carbonate. It was recovered unchanged after boiling for 2 hours with dilute alkali and alcoholic potash [86] On heating with

phosphorous oxychloride it furnished ethyl 2-chloro-4-methylthiazole-5-carb-oxylate (*vide infra*).

Ethyl 2-hydroxy-4-methylthiazole-5-carboxylate (?), m.p 128° —The preparation of this compound is not given in detail in literature [26] It was prepared by the following method ·

Ammonium thiocyanate (6 g.) in alcohol (15 c.c.) was treated with ethyl α-chloroacetoacetate (6·9 g.) in the cold and the mixture allowed to stand overnight at room temperature After refluxing for 15 minutes it was diluted with water (60 c.c.), the sticky solid that had separated filtered off, washed with water and dried On shaking with ether a crystalline product was extracted which melted at 128° after recrystallisation from a mixture of benzene and ligroin (yield 1 g.).

Use of barium thiocyanate in the place of ammonium thiocyanate did not improve the yield of the product. This compound, m.p 128°, on treatment with phosphorus oxychloride did not yield ethyl 2-chloro-4-methyl-thiazole-5-carboxylate

2-Hydroxy-4-methyl-5-acetylthiazole—Chloracetylacetone (13 5 g of b.p. 150–59°) was added in small portions to a cold solution of freshly prepared ammonium thiocarbamate (9 4 g) in water (10 c.c.) The reaction was spontaneous with much effervescence and ice bits were added to control the reaction After setting aside overnight, the crystalline solid that had separated was filtered washed with ice-water and finally with ether to free from traces of the chloroketone and oily impurities The dried solid (7·5 g.) on crystallisation from boiling water separated in colourless elongated rods melting at 210–12° (Found : N 8 99: $C_6H_7O_2NS$ requires N 8 92 per cent.) The acetyl derivative yielded a semicarbazone m.p 240–44° Nagasawa[31] gives the m p 210 5° for 2-hydroxy-4-methyl-5-acetylthiazole (prepared from 2-hydroxy-4-methylthiazole by Friedel-Craft's reaction) and m p 244° for the semicarbazone.

Action of Barium thiocyanate on Chloracetylacetone.—Barium thio-cyanate (7·7 g.) in alcohol (10 c.c.) was mixed with chloracetylacetone (6 75 g.). The reaction was imminent and the mixture set to a thick mass After adding some more alcohol (15 c c.) the mixture was allowed to stand for one hour. The brownish mass was diluted with water, filtered, washed with water and dried (yield, 5 g) On crystallisation from excess of alco-hol the product decomposed at 228° (sintering from 200°). Mixed m.p with the 2-hydroxy-4-methyl-5-acetylthiazole, 150-160°. (Found : N, 9 07 $C_6H_7O_2NS$ requires N, 8·92 per cent.) On boiling with dilute hydrochlo-ric acid, the substance appears to undergo some change but no tangible product could be isolated.

A3

2-Hydroxy-4-thiocyanomethylthiazole.—Ammonium thiocyanate (5 g.) in alcohol (10 c.c.) was treated with α:γ-dichloroacetone (5 g.) under cooling. After adding a few bits of ice, the mixture was allowed to stand overnight. The crystalline product that had separated was filtered off, washed, dried, and extracted with hot benzene. The benzene extract yielded a crystalline product (4 g.), m.p. 95° On crystallising from alcohol, it separated in rectangular plates and had m.p 98·5°. (Found· N. 16·22; C₆H₄N₂OS₂ requires N, 16·28 per cent.) By using 7 g. of potassium thiocyanate and 4 3 g of dichloracetone a purer product weighing 5·6 g was obtained.

2-Hydroxy-4-chloromethylthiazole (IV)—Ammonium thiocarbamate (8·5 g.) suspended in alcohol (15 c.c.) was reacted with α:γ-dichloroacetone (12 g.) under cooling. The dark brownish product that separated on allowing to stand overnight was filtered, washed with water and dried (yield, 12 g.). Hot benzene extracted from the above a colourless crystalline product (3 g.) m.p. 151–52°. turning brownish at 110° (Found· N, 9·68; 9·30; C₄H₄ONSCl requires N, 9 37 per cent) It dissolves in dilute alkali. The residue after the separation of this product was a dark resinous mass, m p. 75–90° difficult to purify

2-Chloro-4 : 5-dimethylthiazole.—(ɪ)   2-Hydroxy-4 : 5-dimethylthiazole (10 g) was gently refluxed with phosphorous oxychloride (30 c.c.) for about 2 hours, the excess of phosphorous oxychloride distilled off (15 c.c) and the residue after decomposition with ice water was steam distilled; 9 c.c. (11·2 g.) of a colourless oil passed over which was separated, dried and distilled; b.p. 190–92°. (Found: N, 9·57; C₅H₆NSCl requires N, 9·49 per cent.).

(ɪɪ) Dry hydrogen chloride was passed into an ethereal solution of α-thiocyanomethylethylketone (9 5 g prepared as described before) for about 4 hours The white crystalline product that separated gradually filled the flask. After removing the ether and the acid fumes, the contents were diluted with water and the oily layer taken up in ether After a thorough extraction with alkali (100 c c of N NaOH), the ethereal solution was dried and the solvent removed. The residue (6 g.) distilled at 185–90° and was found to be 2-chloro-4:5-dimethylthiazole

The same chlorothiazole compound was obtained by treating α-thiocyanomethylethylketone with phosphorous oxychloride for 2 hours under reflux.

Ethyl 2-chloro-4-methylthiazole-5-carboxylate.—Ethyl 2-hydroxy-4-methylthiazole-5-carboxylate (10 g., m.p. 175°) was gently refluxed with phosphorous oxychloride (25 c.c) for 3 hours. Part of the excess of the oxy-

chloride was distilled off and the residue decomposed with water. The solid was taken up in ether (charcoal) and from the extract 9 g. of 2-chloro-4-methylthiazole-5-carboxylate, m.p. 48–51°, was obtained.

We thank Lt.-Col. S. S. Sokhey, Director, for his kind interest in these investigations and also the Lady Tata Memorial Trust for the award of a Scholarship to one of us (A.V.).

SUMMARY

Three methods of synthesising thiazole derivatives unsubstituted in position 2 of the thiazole ring have been investigated to ascertain their scope. The reactions involving the condensation of thioformamide with α-halogenoketones are best effected by treating the halogenoketones with a mixture of formamide and phosphorous pentasulphide; syntheses of 4-methylthiazole, 4:5-dimethylthiazole, 4-methyl-5-acetylthiazole and ethyl 4-methylthiazole-5-carboxylate are described as examples. By this method thiazole and ethyl thiazole-4-carboxylate could not be prepared.

2-Aminothiazole, the 5-methyl and 5-ethyl derivatives have been converted into the corresponding 2-chloro and 2-bromo derivatives in good yields by diazotising the aminothiazoles in a mixture of phosphoric acid and nitric acid or about 45 per cent. sulphuric acid and treating the diazonium products with an aqueous solution of copper sulphate and sodium halide. Treatment of the diazonium solutions with cuprous oxide in alcohol or calcium hypophosphite yielded the deaminated products, the latter giving better yields than the former reagent. These reactions are not of universal applicability and their scope has been ascertained by studying them in a number of cases 2-Chloro-5-nitrothiazole and 2-bromo-5-nitrothiazole have been prepared by diazotising 2-amino-5-nitrothiazole in dilute sulphuric acid containing copper-sulphate and the sodium halide.

The preparation of 2-hydroxythiazole derivatives by condensing α-halogenoketone with either the thiocyanates or ammonium thiocarbamate has been studied using chloracetone, dichloracetone, α-chloromethylethylketone, chloracetylacetone and ethyl α-chloroacetoacetate. In the case of the chloroderivatives of β-ketonic ester and β-diketone, ammonium thiocarbamate yields the expected 2-hydroxy thiazole derivative while the product obtained using the thiocyanates is of doubtful constitution. The 2-hydroxythiazol compounds could be converted into the 2-chlorothiazole in good yields by treating with phosphorous oxychloride. Saturation of α-thiocyanomethylethylketone with hydrogen chloride furnished 2-chloro-4:5-dimethylthiazole.

REFERENCES

1	Boon, W R	Brit Patent, 546,994 , C. A , 1943, 37, 5556.
2	Miolati, A.	Gazzetta, 1893, 23, I, 578.
	Levi, T. G.	Ibid , 1931, 61, 719.
3	Gabriel, S	Ber , 1910, 43, 134, 1283
	Rudenberg, K	Ibid., 1913, 46, 3555
	Bachstez, M	Ibid , 1914, 47, 3163
	Miyamichi, E	J Pharm. Soc Japan, 1926, No 528, 103 ; C A , 1926, 20, 2679
4	Hromatka, O	Ger Patent 670, 131 , C. A , 1939, 33, 2909.
5	Buchman, Reims and Sargent	J Org Chem , 1941, 6, 764
6.	Schatzmann, P.	Annalen, 1891, 261, 10.
7	McLean and Muir	J Chem Soc., 1942, 383
8	Erlenmeyer and Morel	Helv chim Acta, 1942, 25, 1073
9	Schoutissen, H A	J Amer Chem Soc , 1933, 55, 4531
10	Walker and Hodgson	J Chem Soc., 1933, 1620
11	Morgan nad Morrow	Ibid., 1915, 107, 1294
12	Hodgson, Birtnell and Walker	Ibid , 1941, 770
13	————————	Ibid , 1944, 18
14.	Popp, G	Annalen, 1889, 250, 274
15	Hodgson and Turner	J Chem Soc , 1943, 86 ; 1942, 748
16	Mai, J	Ber , 1902, 35, 162
17	Adams and Kornblum	J Amer Chem Soc , 1941, 63, 192
18	Brewster and Poje	Ibid , 1939, 61, 2418
19	Arapides, L	Annalen, 1888, 249, 14.
20	Andersag and Westphall	Ber , 1937, 70, 2035
21	Marchesini, G	Gazzetta, 1893, 23, II, 442
22	Hantzsch, A	Ber , 1927, 60, 2537 . 1887, 20, 3127
23	Tcherniac, J	Ibid , 1892, 25, 3648, 2619
24	————————	J Chem Soc , 1919, 115, 1072
25	Hantzsch, A	Ber , 1928, 61, 1776
26	——— and Weber	Ibid , 1887, 20, 3131
27	Ganapathi Shirsat and Dehwala	Indian Patent 29345
28	——— and Venkataraman	Proc Ind Acad Sci , 1945, 22 A, 359
29	Tomlison, M L	J Chem Soc , 1935, 1030
	Harrington and Moggridge	Ibid , 1939, 443
	Clark and Gurin	J Amer Chem Soc , 1935, 57, 1876
	Buchman and Richardson	Ibid , 1939, 61, 892
30	Baumgarten, Dornov, Gutschmidt and Krahl	Ber , 1942, 75, 442 , C. A , 1943, 37, 3091
31	Nagasawa, H	J. Pharm Soc Japan, 1938, 59, 471 ; C. A., 1940, 34, 102.

CALCULATION OF THE INFRA-RED ACTIVE AND RAMAN INACTIVE FREQUENCIES OF α QUARTZ

By BISHAMBHAR DAYAL SAKSENA

(Department of Physics, University of Allahabad)

INTRODUCTION

THE author (1940) has shown by an experimental and theoretical study that α quartz has 16 fundamental frequencies which can be divided into three classes, A, B and E class—A being totally symmetric, class B anti-symmetric and class E doubly degenerate   Four frequencies namely 207, 356, 466, 1082 fall in class A and are Raman active and infra-red inactive   Four others namely 364, 508, 777, 1149 fall in class B and are Raman inactive and infra-red active but only in the extraordinary ray   The remaining eight frequencies falling in class E are doubly degenerate and are both Raman active and infra-red active but only in the ordinary ray   These frequencies explain the specific heat of α quartz between 23°A and 808°A with a fair degree of accuracy   In later papers the author (1942, 1944) has calculated, with the help of the four totally symmetric frequencies, the force-constants in α quartz and also the ‘elastic constants.   The force constants calculated are those of Si-O valence (K), O—O repulsion (K_3), Si $\diagdown$ O — Si deformation (K_1) and O $\diagdown$ Si—O deformation (K_4). These are shown in Table I.

TABLE I

$K_z \times 10^{-5}$	$K_1 \times 10^{14}$	$K_3 \times 10^{13}$	$K_4 \times 10^{5}$	Calculated values of Raman frequencies				$C_{11} \times 10^{-11}$	$C_{12} \times 10^{-11}$	$C_{13} \times 10^{-11}$	$C_{33} \times 10^{-11}$	$C_{44} \times 10^{-11}$	$C_{11} \times 10^{-11}$	$C_* \times 10^{-11}$	$\eta \times 10^{-11}$
4·98	·454	1·565	−·892	1087	491	333	198	12·3	−·64	·65	12·0	8·5	1·30	6·4	4·47
5·01	1·056	1·316	−·8992	1087	506	310	195	11·3	−·44	1·40	10·5	8·4	1·59	5·87	4·38
Observed values				1082	466	356	207	8·68	73	1·41	10·5	5·82	1·73	3·98	3·85

It is the purpose of the present note to calculate with the help of the above force-constants the four frequencies belonging to class B which are Raman inactive and infra-red active but only in the ordinary ray.

379

2. Symmetry Modes and Potential Energy Function

The method of procedure is just the same as described in earlier papers For the sake of diagram reference may be made to Fig. 1 in an earlier paper of the author (1944) The symmetry co-ordinates of the four modes have been worked by the author in an earlier paper and are given below:—

$$m_0^{\frac{1}{2}} (z_1 + z_2 + z_3 + z_4 + z_5 + z_6) - m^{\frac{1}{2}}_{S_1} (z_7 + z_8 + z_9 + z_{10} + z_{11} + z_{12}) \quad \text{(I)}$$

$$y_2 + y_4 + y_6 - y_1 - y_3 - y_5 \quad \text{(II)}$$

$$y_8 + y_{10} + y_{12} + y_7 + y_9 + y_{11} \quad \text{(III)}$$

$$x_7 + x_9 + x_{11} - x_8 - x_{10} - x_{12} \quad \text{(IV)}$$

As the silicon atom pairs (1, 4), (3, 6) and (2, 5) have the same motions at any given instant the symmetry co-ordinates (I) and (II) are to be written in the form shown. The letters x_i, y_i, z_i represent motions of the ith atom from its position of rest as origin. Each x_i is directed towards a plane in the basal plane containing the given atom where the three-fold axis meets it, z_i is perpendicular to the basal plane and positive upwards, y_i is at right angles to both so as to make the motion right handed. If α, β, γ, δ are the displacements in the four modes respectively, the variations of Si—O distances, O—O distance and Si $\diagdown_{\text{O—Si}}$ and O $\diagdown_{\text{Si—O}}$ angles can be calculated. As each Si atom is shared by two cells, 24 Si—O distances, 36 O—O distances and 36 O $\diagdown_{\text{Si—O}}$ angles and 6 Si $\diagdown_{\text{O—Si}}$ angles are to be considered for each cell.

The variations of Si—O distances ($\triangle \gamma$), the variation of O—O distances ($\triangle R$) and the variations of O $\diagdown_{\text{Si—O}}$ angles ($\triangle \phi$) for Si atom 1 are given below and these are the same for the remaining Silicon atoms (2, 3, 4, 5, 6).

$$\triangle \gamma_{1,7} = - \triangle \gamma_{1,12} = \frac{- \cdot 1672\delta - 1 \cdot 447\gamma - 1 \cdot 214\beta + 1 \cdot 311\dot{a}}{1 \cdot 588}$$

$$\triangle \gamma_{1,9} = - \triangle \gamma_{1,10} = \frac{\cdot 5963\delta + 8935\gamma - 6384\beta - 2 \cdot 431\alpha}{1 \cdot 588}$$

$$\triangle R_{7,12} = \triangle R_{9,10} = 0$$

$$\triangle R_{7,10} = - \triangle R_{12,9} = \frac{- 8604\delta - 4 \cdot 800\gamma}{2 \cdot 55}$$

$$\triangle R_{7,9} = - \triangle R_{12,10} = \frac{2 \cdot 669\delta - 1 \cdot 49\gamma}{2 \cdot 52}$$

$$\triangle \phi_{7,1\,12} = \triangle \phi_{9,1,10} = 0$$

$$\Delta \phi_{7,1,10_i} = - \Delta \phi_{9_i,1,12} = \frac{\cdot 12548 - 1 \cdot 776\gamma + \cdot 743\beta - 4 \cdot 833\alpha}{2 \cdot 414}$$

$$\Delta \phi_{7,1,9_i} = - \Delta \phi_{12_i,1,10_i} = \frac{2 \cdot 1298 - \cdot 7934\gamma + 2 \cdot 334\beta + 1 \cdot 41\alpha}{2 \cdot 436}$$

The variations of $Si\diagdown O\diagup Si$ angles $(\Delta \varPhi)$ are given by

$$\Delta \varPhi_{9,7,1} = - \Delta \varPhi_{12,6,1} = \Delta \varPhi_{6,11,5} = - \Delta \varPhi_{\prime,10,4} = - \Delta \varPhi_{4,9,3} = - \Delta \varPhi_{3,8,2}$$
$$= - \frac{\cdot 7909\delta + 1 \cdot 02\gamma - \cdot 810\beta + 2 \cdot 065\alpha}{1 \cdot 355}$$

The potential energy is given by

$$2V = \tfrac{1}{2} \underset{24}{\varSigma} K (\Delta \gamma_i)^2 + \underset{6}{\varSigma} K_1 (\Delta \varPhi_i)^2 + \tfrac{1}{2} \underset{36}{\varSigma} K_2 (\Delta \phi_i)^2 + \tfrac{1}{2} \underset{36}{\varSigma} K_3 (\Delta R_i)^2$$

On expanding it becomes

$$2V = 6 \left[a\delta^2 + b\gamma^2 + c\beta^2 + d\alpha^2 + 2e \,\delta\gamma + 2f \,\delta\beta + 2g \,\delta\alpha + 2h \,\gamma\beta \right.$$
$$\left. + 2i \,\gamma\alpha + 2j \,\alpha\beta \right]$$

where $a = \cdot 1519 \,K + \cdot 3407 \,K_1 + \cdot 7662 \,K_2 + 1 \cdot 237 \,K_3$

$b = 1 \cdot 147 \,K + \cdot 5667 \,K_1 + 6475 \,K_2 + 3 \cdot 888 \,K_3$

$c = \cdot 7460 \,K + \cdot 3574 \,K_1 + 1 \,013 \,K_3$

$d = 3 \cdot 025 \,K + 2 \cdot 322 \,K_1 + 4 \cdot 343 \,K_2$

$e = \cdot 3072 \,K - \cdot 4394 \,K_1 - \cdot 3227 \,K_2 + \cdot 0083 \,K_3$

$f = - \cdot 0706 \,K + \cdot 3489 \,K_1 + \cdot 8531 \,K_2$

$g = - \cdot 6614 \,K - \cdot 8898 \,K_1 + \cdot 4018 \,K_2$

$h = \cdot 4703 \,K - \cdot 4501 \,K_1 - \cdot 5386 \,K_2$

$i = - 1 \cdot 614 \,K + 1 \cdot 148 \,K_1 + 1 \cdot 285 \,K_2$

$j = - \cdot 0154 \,K - \cdot 9114 \,K_1 - \cdot 0617 \,K_2$

The kinetic energy is given by

$$6m_0 \,\dot{\delta}^2 + 6m_0 \,\dot{\gamma}^2 + \tfrac{1}{2} \times 6m_{s_i} \,\dot{\beta}^2 + 6m_0 \left(\frac{m_{s_i}}{m_0}\right) \dot{\alpha}^2 + \tfrac{1}{2} \times 6m_{s_i} \left(\frac{m_0}{m_{s_i}}\right) \dot{\alpha}^2$$

$$= 6 \left[16\dot{\delta}^2 + 16\dot{\gamma}^2 + 14 \cdot 15\dot{\beta}^2 + 36 \cdot 3\dot{\alpha}^2 \right]$$

The frequencies are given by the determinant

$$\begin{vmatrix} a - 16\lambda^2 & e & f & g \\ e & b - 16\lambda^2 & h & i \\ f & h & c - 14 \cdot 15\lambda^2 & J \\ g & i & j & d - 36 \cdot 3\lambda^2 \end{vmatrix} = 0$$

SYNTHESIS OF IZALPININ

By K. Visweswara Rao and T. R. Seshadri, F.A.Sc.

(From the Department of Chemistry, Andhra University)

IZALPININ was isolated from the seeds of *Alpinea japonica* by Kimura and Hoshi[1] and its constitution was based on the following considerations It has the molecular formula $C_{16}H_{12}O_5$ and contains one methoxyl group On demethylation it yields nor-izalpinin identical with galangin and on methylation forms galangin-trimethyl ether It contains a hydroxyl group resistant to methylation and it is different from the 3-methyl ether of galangin It was, therefore, concluded to be galangin 7-methyl ether, *i.e.*, 7-methoxy-3, 5-dihydroxy-flavone Excepting the prep ration of 3 5. 7-trimethoxy flavone which was shown to be identical with the dimethyl ether of izalpinin no further synthetic proof was advanced by the above authors Since no method is available for the direct synthesis of izalpinin, it has now been obtained by the partial demethylation of the di- and tri-methyl ethers of galangin by means of anhydrous aluminium chloride and bromide.
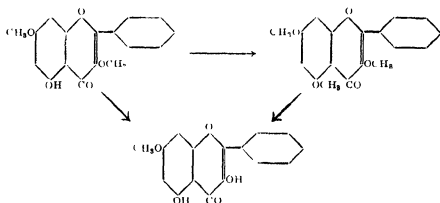
Partial demethylation with aluminium chloride was investigated in the past using several methoxy-flavones and it was established that the reagent affects the 5-methoxyl group alone Employing this, tectochrysin,[2] genkwanin,[3] 8-methyl ether of primetin,[4] primetin[5] and wogonin[6] have been prepared The use of this reagent was extended to the field of methylated flavonols by Krishnaswamy and Seshadri.[7] Their experiments showed that like the 5-methoxyl, the 3-methoxy-group also underwent demethylation preferentially.

The action of aluminium bromide as a demethylating agent has not been studied so far in the flavone and flavonol series. Its higher solubility and greater reactivity as compared with the chloride are advantages in its favour. Consequently experiments have now been carried out on the methyl ethers of galangin using this reagent also.

Tasaki[8] who first reported the preparation of the trimethyl ether of galangin gave the melting point as 165–66°. But, later, Kimura and Hoshi[1] who prepared it by condensing $\omega \cdot 4 \cdot 6$-trimethoxy-2-hydroxy-acetophenone (obtained by the fission of hexamethyl myricetin) with benzoic anhydride and sodium benzoate described it as light brown hexahedral prisms melting at 195–96° On repeating the experiment Kimura and Hoshi using a synthetic sample of the above ketone, the product obtained was not the expected $3 \cdot 5 \cdot 7$-trimethoxy-flavone. It was yellow, gave a greenish brown colour with ferric chloride in alcoholic solution and melted at 144–46° thus agreeing with $3 \cdot 7$-dimethoxy-5-hydroxy-flavone obtained by methylating galangin with methyl iodide. The presence of the 5-hydroxyl was confirmed by the preparation of the acetate and also by further methylation to $3 \cdot 5 \cdot 7$-trimethoxy-flavone. This trimethyl ether has now been obtained as colourless hexahedral prisms melting at 199–200°. It is, therefore, evident that during the above Allan-Robinson condensation demethylation has taken place. Similar cases were noted in the flavone series by Wesseley and Moser[9] and by Baker et al.[10] Such demethylation does not seem to be taking place as a rule though the possibility exists definitely. Our observation recorded above appears to be the first example in the flavonol series. More cases have been met with in the course of similar work in these laboratories.

The demethylation of $3 \cdot 7$-dimethoxy-5-hydroxy-flavone and $3 \cdot 5 \cdot 7$-trimethoxy flavone has now been effected in nitrobenzene solution at 100° with aluminium chloride; izalpinin is obtained in good yield in both cases. The action of aluminium bromide has been investigated under two different conditions (1) at 100° for 1 hour and (2) at the laboratory temperature for 12 hours using again nitrobenzene as the solvent and the compounds mentioned below; the same products are obtained under both conditions. 5:7-Dihydroxy-3-methoxy flavone yields galangin, $3 \cdot 7$-dimethoxy-5-hydroxy-flavone and $3 \cdot 5 \cdot 7$-trimethoxyflavone yield izalpinin. It has been the practice to remove the solvent by steam distillation but this leads to considerable decomposition yielding resinous products. A simpler and more convenient method has now been adopted. It involves the use of petroleum ether which dissolves and removes nitrobenzene leaving behind the aluminium halide complex which can be conveniently decomposed later on.

Izalpinin obtained synthetically by the above methods has all the properties attributed to the natural sample. One property has now been observed and which distinguishes it from galangin is its insolubility in aqueous sodium carbonate. Galangin is soluble in this reagent. This observation will be useful for separating a mixture of the two when occurring in nature. The acetate of izalpinin has also been prepared and described.

EXPERIMENTAL

3 : 7-Dimethoxy-5-hydroxy-flavone:—ω : 4 : 6-Trimethoxy-2-hydroxy-acetophenone was prepared according to the method of Row and Seshadri,[11] effecting partial methylation of ω-methoxy phloracetophenone.

An intimate mixture of this ketone (2 g.), benzoic anhydride (8 g.) and sodium benzoate (2 g.) was heated under vacuum at 170–80° for 4–5 hours. It was then cooled and the product boiled with alcoholic potash (40 c.c. of 10% solution) for 20 min. The alcohol was then removed under reduced pressure and the residue treated with water (100 c c.) The yellowish brown solid was filtered and washed with water (fraction I). The filtrate, on saturation with carbon dioxide, yielded a brown solid which was also filtered and washed with water (fraction II).

Fraction I was crystallised from acetic acid when an yellow shining crystalline solid (needles) melting at 142–45° was obtained. A second crystallisation from alcohol gave a product melting sharp at 145–46°. Fraction II was similarly crystallised. It was also obtained as yellow needles melting at 145–46° (m.p. of galangin dimethyl ether reported by Perkin and Everest,[12] 142°). It was found to be identical with fraction I and the mixed melting point was not depressed. (Found· C, 68·0; H, 4·5; $C_{17}H_{14}O_5$ requires C, 68·4; H, 4·7%.) The flavone was sparingly soluble in aqueous alkali. In alcoholic solution it gave an olive brown colour with ferric chloride. Yield, 1·5 g.

A search was made for the trimethyl ether in the mother-liquors obtained from the crystallisation of fraction I On evaporation to dryness a dark brown residue was obtained. When crystallised from alcohol twice a very small quantity of an yellow solid melting indefinitely between 130–60° was obtained. It also gave a brown colour with ferric chloride. The quantity was too small to enable further study. It appeared that there was no significant amount of the trimethyl ether.

*3 : 7-Dimethoxy-5-acetoxy flavone:—*3 : 7-Dimethoxy-5-hydroxy flavone (0·1 g.) was acetylated by boiling with acetic anhydride (3 c c.) and sodium acetate (0·5 g.) for 2 hours. The white solid obtained on pouring the

reaction mixture into ice-water was filtered, washed and crystallised twice from alcohol. It came out in the form of fine colourless silky needles melting at 175–76°. It gave no colour with ferric chloride. (Found: C, 66·7; H, 4·5; $C_{19}H_{18}O_6$ requires C, 67·0; H, 4·7%.)

3 : 5 : 7-*Trimethoxy-flavone : I Method:*—A solution of 3 : 7-dimethoxy-5-hydroxy-flavone (0·5 g.) in anhydrous acetone (50 c.c.) was treated with dimethyl sulphate (0·5 c.c.) and freshly ignited potassium carbonate (3 g.). After refluxing for 12 hours, the potassium salts were filtered off and the filtrate evaporated when the trimethyl ether was left behind as a crystalline solid. It was purified by crystallising twice from alcohol when it came out as big colourless hexahedral prisms melting at 199–200°. It was insoluble in aqueous alkali and gave no colour with alcoholic ferric chloride (Found: C, 69·2; H, 4 8; $C_{18}H_{16}O_5$ requires C, 69 2; H, 5·1%.) Yield, 0·5 g.

II Method:—5 . 7-Dihydroxy-3-methoxy flavone (1 5 g.) (prepared according to Kalff and Robinson[1]) was methylated in anhydrous acetone solution (200 c.c.) with dimethyl sulphate (2 c.c.) and anhydrous potassium carbonate (10 g.). The trimethyl ether was purified by crystallisation from alcohol Yield, 1·4 g. It was identical with the sample obtained from the first method and the mixed melting point was undepressed.

Preparation of Izalpinin.

Demethylation of (1) *galangin-dimethyl-ether:* (a) *Aluminium chloride method:*—A solution of 3 : 7-dimethoxy-5-hydroxy-flavone (0·5 g.) in dry nitrobenzene (10 c.c.) was treated with a solution of anhydrous aluminium chloride (1 g.) in the same solvent (5 c c.) with cooling. The dark coloured solution was kept on a boiling water-bath for 45 minutes and cooled. Ice-cold hydrochloric acid (20 c.c. of 1 : 1 acid) was then added with cooling and the nitrobenzene removed by steam distillation. The dark brown residue was crystallised from alcohol when a yellowish brown solid was obtained which melted at 185-90° with sintering at 178°. A second crystallisation raised the melting point to 190–93°, with slight sintering at 188°. After a third crystallisation from alcohol izalpinin came out as pale yellow lance-shaped plates melting at 194–95°. The yield of the pure product was 0·15 g. It was easily soluble in aqueous alkali to a bright yellow coloured solution and it gave a brown colour with ferric chloride in alcoholic solution

(b) *Aluminium bromide method:*—A solution of 3 : 7-dimethoxy-5-hydroxy flavone (0 3 g.) in dry nitrobenzene (8 c.c.) was treated with anhydrous aluminium bromide (0·5 g.); the solution was kept at 100° for 1 hour and then cooled Excess of petroleum ether was added, the contents

were shaken well and allowed to stand for 5 minutes. The clear upper layer of liquid was decanted off from the brown semi-solid of the aluminium bromide complex. The latter was washed thrice again with petroleum ether and was then decomposed by adding small pieces of ice and hydrochloric acid (20 c.c. of 1 : 1 acid). After keeping for 2–3 hours the yellow solid was filtered and washed with water and a little petroleum ether On crystallisation from alcohol it came out as yellow short lance-shaped plates melting at 190–93°. A second crystallisation gave the pure product melting at 194–95°. It was identical with the sample obtained above. Yield, 0·22 g.

(2) *Galangin-trimethyl ether* · (a) *Aluminium chloride method:*—A solution of 3 : 5 : 7-trimethoxy-flavone (0 5 g.) in dry nitrobenzene (10 c.c.) was treated with aluminium chloride (1 g.) in the same solvent. The mixture was kept at 100° for one hour and then cooled. The solvent was then removed by means of petroleum ether and the residue treated with water and concentrated hydrochloric acid. The final decomposition of the product was effected by heating the mixture on the water-bath for 10 minutes. The resulting yellow solid was filtered, washed with water and crystallised from ethyl acetate. Izalpinin came out in the form of yellow rectangular prisms melting at 194–95°. Yield, 0 4 g.

(b) *Aluminium bromide method* ·—3 : 5 : 7-Trimethoxy-flavone (0 5 g.) was treated with aluminium bromide (1 g.) in dry nitrobenzene (15 c.c) and the solution kept at the laboratory temperature for 12 hours The solvent was then removed with the help of petroleum ether and the complex decomposed in the manner described above The product, on crystallisation successively from alcohol and dilute acetic acid, came out as glistening lance-shaped plates melting at 194–95°. It was identical with the samples obtained by the above methods. Yield 0·4 g

The above experiment was repeated using a temperature of 100° for 45 minutes for the demethylation: the yield and purity of izalpinin were just the same. (Found: C, 67·9; H, 4·3, OCH_3 10·9, 11·1; $C_{16}H_{12}O_5$ requires C, 67·6; H. 4 3; OCH_3, 10·9%.)

Izalpinin acetate:—Izalpinin (0 4 g.) was boiled for 2 hours with acetic anhydride (5 c.c.) and anhydrous pyridine (2 drops) The solid that separated out on pouring the reaction mixture into ice-water, was extracted with ether and the ether solution shaken with cold aqueous sodium bicarbonate to remove acetic acid. The solvent was evaporated and the colourless residue was first crystallised from alcohol and subsequently from benzene-petroleum ether mixture. The acetate was thus obtained as colourless, long rectangular prisms melting at 172–73°. The yield was almost quantitative.

The mixed melting point with 3 : 7-dimethoxy-5-acetoxy flavone was considerably depressed (150–55°). (Found: C, 65·4; H, 4·6; $C_{20}H_{16}O_7$ requires C, 65·2; H, 4·3%.)

A solution of izalpinin acetate (0·25 g.) in alcohol (10 c.c.) was treated with concentrated hydrochloric acid (2 c.c.) and the solution kept boiling for 10 minutes. The yellow crystalline solid that separated out was filtered, washed with water and recrystallised from alcohol when it came out as yellow lance-shaped plates melting at 194–95°. It was identical with the original sample of izalpinin and the mixed melting point was undepressed.

SUMMARY

Izalpinin (7-methyl ether of galangin) has been obtained by the demethylation of galangin di- and trimethyl ethers using both aluminium chloride and aluminium bromide. The synthetic sample has all the properties recorded for the naturally occurring substance. The condensation of ω : 4 : 6-trimethoxy-phloroacetophenone with benzoic anhydride and sodium benzoate yields mainly 3 : 7-dimethyl ether of galangin.

REFERENCES

1	Kimura and Hoshi	.	Chem Abs , 1937, 31, 6654
2	Gulati and Venkataraman	.	J C S , 1936, 267
3	Mahal and Venkataraman.		Ibid , 1936, 569
4	Baker, Brown and Scott		Ibid , 1939, 1922.
5	Nakazawa		Chem Abs , 1940, 34, 1017
6	Shah, Mehta and Wheeler		J C S., 1938, 1555.
7.	Krishnaswamy and Seshadri		Proc Ind Acad Sci., A, 1942, 15, 437
8.	Tasaki		Chem Abs , 1926, 20, 1990
9.	Wesseley and Moser	.	Monatsh, 1932, 60, 26
10.	Baker		J C. S., 1939, 956.
11	Row and Seshadri	.	Proc Ind Acad Sci , under publication
12	Perkin and Everest	.	" Natural Organic Colouring Matters", p 177.
13	Kaliff and Robinson	.	J C.S , 1925, 181.

THE THRESHOLD POTENTIAL, *LIGHT-EFFECT* AND CHEMICAL REACTIVITY UNDER ELECTRICAL DISCHARGE

By S. S. JOSHI

(Chemistry Department, Benares Hindu University)

THE fundamental importance of the minimum threshold potential V_m[1] (*vide infra*) as a determinant of the rate and nature of a chemical or quasi-chemical change under electrical discharge (Joshi, 1929; 1931); and that the ' electron affinity ' of the excited gas affects V_m (Joshi, *ibid.*), is shown by the results of numerous discharge reactions[2,3,4,5,6,7] investigated in these Laboratories under various conditions; different temperatures, external irradiation and magnetic field Amongst these findings, which more than suggested the new *light-effect*,* was the following result observed in the hydrogen-chlorine combination under the silent discharge.[3] Whilst, in conformity with other discharge reactions, this one set in, only when the applied potential V exceeded the minimum threshold potential V_m[6,9] (which is characteristic of the nature of the change, of the operative conditions and may be identified, or related simply with the corresponding Paschen potential especially in elementary gases),[6,9] the direction of the corresponding current change, produced at a constant V, namely a continuous *decrease* during the progress of this reaction, was apparently contrary to an earlier theoretical result (Joshi, 1929; 1931) found to be in accord with numerous experimental observations,[2,3,4,5,6,7,8,9] it was that *ceteris paribus*, the occurrence of an intermediate or/and final product with an ' electron affinity ' greater than that of the antecedent material, should lead to a decrease of the corresponding current flowing through the system,[1] and *vice versa*. In the present instance, a reversal of the reaction is considered inappreciable due to the marked stability of the final product HCl under the silent discharge; also the constancy of pressure of the reaction mixture observed over a wide range of conditions indicated that the stoicheometric equation represents the chief mechanism of the reaction. The electron affinity of chlorine (presumably dissociated appreciably into atoms under the discharge) is

---

* A decrease due to irradiation of the current i in chlorine and some other gases under electrical discharge. This phenomenon was first reported by the author during lectures on " Molecular Activation " at the University of Lucknow in November 1938, Prof. B Sahni, F.R.S., presiding

389

considerably greater than that of HCl; since the concentration of the latter increases progressively during the change at the cost of chlorine a decrease of i during the above reaction appeared anomalous

Observation under silent discharge of the sudden inception of photographic activity at V_m[1,2]; and further of the decrease of i during the hydrogen-chlorine combination[3] under the silent discharge alone, that is, in dark; and also that under the simultaneous action of the silent discharge and external light, the above decrease of i was more pronounced, suggested that the production of a glow in the mixture, feeble at V_m and of greater intensity at higher V may be presumed This led to the finding that the V_m for pure chlorine is *increased* by exposure to light.[4] From this, a current decrease $\triangle i$, consequent on irradiation was expected, since in general V-V_m determines i.[1,5,6] This predicted *light-effect* has now been observed in all parts of the spectrum from the red to X-rays[7,8,9] Under favourable conditions this *light-effect* corresponds to as high as 93 to 95 per cent of an almost instantaneous and reversible decrease of the original current i in the dark[8]

That, *ceteris paribus*, the relative *light-effect* decreases as the input frequency (*i.e.* of the A C supply) is increased, it is a general characteristic of this phenomenon I have recently observed that an appreciable *light-effect* is produced in a chlorine filled semi-ozoniser, energised by fields due to (not smoothed unidirectional potentials The resulting current due to the discharge i, however, is in general of the pulsating type, as is to be anticipated from general considerations. The actual current structure and its time-delineation in a given discharge would depend upon the nature of the excited system, the threshold potential V_{m}, impedance, the 'time-constant' of the circuit, etc Compared with the photo-electric effect under ordinary conditions, the present phenomenon would appear to be better adapted for the familiar amplifier devices, owing to the circumstance that the discharge current i is not stationary

Results of detailed investigations in these Laboratories have established that this phenomenon is not detected below V_m,[8,9,10] under intense irradiation (including the ultra-violet) even within the absorption band of chlorine and large displacement currents obtained with high frequencies input to the system. This, in part, discriminates the *light-effect* $\triangle i$ from the well-known Budde effect; other points of contrast and similarity between these two phenomena are discussed elsewhere[7] The latter denotes the production of a pressure rise on irradiation within the region of characteristic absorption especially in chlorine and in the absence of external electrical field. Fields intense enough for the secondary ionisation of the (irradiated)

gas are, however, necessary for the occurrence of $\triangle i$. No Budde pressure rise (greater than 0·5 mm. in about 200 mm. of gas pressure) was observed in chlorine and other gases under conditions appropriate to the production of a maximum *light-effect*. Budde effect is generally attributed to a warming up of the gas by the heat of the recombination of the atoms, which are produced by irradiation. If the recombination occurs on the container walls, which is to be anticipated in a vessel of a large surface to volume ratio as in a Siemens' type ozoniser, the corresponding heat released must mainly be conducted away by the walls and consequently the Budde expansion may become negligible, as observed under the silent discharge.

It was noticed earlier that as V is increased progressively, whilst $\triangle i$ that is the net change of i increases, % $\triangle i$ which denotes the *light-effect* expressed as a percentage of i diminishes'; at much larger V, even $\triangle i$ is reduced. Subsequent work has shown that this result may be extended to a wider range of conditions. At, and just above the threshold potential V_m, the current is small and markedly unsteady; the corresponding % $\triangle i$, however, is comparatively high. Thus, for example, % $\triangle i$ increased from 23 to 43, as the applied potential was reduced from 12 to 4 kV. Near V_m within 3·3 to 3·6 kV, % $\triangle i$ varied irregularly in the range 46 to 68. That % $\triangle i$ tends to a maximum near V_m would now appear to be a general characteristic of this *light-effect* phenomenon; this has been demonstrated by observations made with different frequency filters, ozonisers, the various A.C. detectors mentioned previously[11] and also from the decrease of the sound emission from a loud speaker actuated by an amplifier introduced in the current circuit[9]; and recently from the remarkably sudden extinction of a neon glow in a Geissler tube or a like contrivance, when coupled with the output circuit of the chlorine tube, when irradiated. It is suspected, however, that these different methods do not correspond to quite the same value of the exciting potential at which % $\triangle i$ is a maximum; this may be inferred from general considerations of the limitations and the distinctive behaviour of the various detectors employed. It was found previously that the introduction of a sensibly non-inductive and non-capacitative resistance in the low tension circuit decreases the corresponding % $\triangle i$, but increases that observed in an aerial.[10] It is significant that this influence of the external resistance is most pronounced near V_m, where the relative *light-effect* % $\triangle i$ is a maximum.[10] This influence of V on the *light-effect* is well brought out by a study of this phenomenon with a cathode-ray oscillograph. A suitable Dubilier type resistance was introduced between the low tension electrode of the ozoniser and the earth. At a given V on the ozoniser, the P.D. developed across this resistance was applied to the deflecting pair of

A4

electrodes in the oscillograph without or with 'gain' as desired; the other pair was connected to the time-sweep potential. Fig. 1 (a) shows a pair of oscillograms at 3·74 kV which is just above the threshold potential V_m (about 3 kV). The decrease on irradiation of the amplitudes of especially the high frequency components is evident; when, however, the applied potential is increased to 13·4 kV [see Fig. 1 (b)] the oscillograms reveal a marked asymmetry between the consecutive (lower and upper) half-waves; their shapes also show that the second and third harmonics are present. Furthermore, the *light-effect* as indicated by the amplitude decrease of the high frequencies is very much less at 13·4 kV than at the lower potential.

At an exciting potential higher than V_m when the current is chiefly of the ohmic or the conductance type, the more so the larger the V, the *light-effect* falls off with V with a rapidity which depends markedly on the nature of the light, the excited gas, its pressure, etc. This *light-effect* is not produced at potentials less than V_m,[9,10] when the conduction is entirely capacitative; furthermore, the production of the *light-effect* is accompanied by a decrease in the corresponding wattage, that is, of the energy dissipated in the system.[9,10] Presumably, therefore, an incipient transition from the purely dielectric to that of the (ohmic) type conduction in the irradiated gas, represents an optimum condition for the production of this phenomenon. This deduction is in agreement with a previous finding that the *light-effect* is greatly diminished on deposition of metallic coats or films on the annular surfaces of the ozoniser.[10] The complete reversibility of this effect not only in respect of the optical factors such as the light-intensity, frequency, etc., but also the electrical factors such as the applied potential, the supply frequency and especially the remarkably small time-lag[8] in its production, suggest that the predominant mechanism of the change is not of the chemical or the normal molecular type, but rather physical, *e.g.*, the ionic or/and the electronic. It is also suggested tentatively that a change caused by light leading to an increase of the 'electron affinity' of the medium may represent an initial stage in the mechanism of the *light-effect*. It was shown previously that V_m increases by increasing the 'electron affinity' of the medium.[1] An increase of V_m, thus caused, would decrease $V-V_m$, and hence the current as observed under light.

It was found over an appreciable range of V, that besides i, the magnitude (in a given time) of a discharge reaction is minimum at V_m, and increases with $V-V_m$[1]; the variation of the relative *light-effect*, however, is opposite Presumably, the high frequencies in i contribute but little to the magnitude of the corresponding discharge reaction of the chemical or molecular type[13]; they represent, however, the main source of the *light-effect*.[9,10,11]

Fig 1 (a)

3 74 kV (r m s), at 50 cycles sec.
Across 10,000 Ω . No gain
Time of Exposure   60 seconds

In dark   With irradiation

Fig 1 (b)

13 4 kV (r m s), at 50 cycles sec
Across 1,000 Ω , Moderate gain
Time of Exposure – 40 seconds
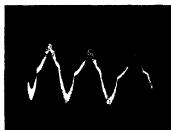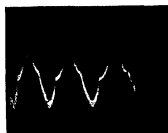
In dark   With irradiation

SUMMARY

From an observation of a photo-increase of the minimum threshold potential V_m, that the current i at a given V should decrease under light was predicted by the author from a finding that i depends upon $V-V_m$. Presumably, the magnitude of a chemical reaction under discharge does not depend appreciably on the corresponding high frequencies produced; these, however, constitute the main source of the *light-effect*. Furthermore, in contrast with a chemical reaction which is minimum at V_m, the *light-effect* observed with a number of A.C. indicators, and expressed as percentage of i is a maximum near V_m. This, together with a general finding that the *light-effect* is not sensible below V_m, suggests that an optimum condition for its occurrence is a transition state, within which the conductivity of the gas changes from the dielectric to the ohmic type. The ' electron affinity ' of the excited gas is another important determinant of this phenomenon.

REFERENCES

1.	Joshi	*Trans. Farad. Soc.*, 1929, **25**, 125–28, 141–43.
	——	*Proc. Indian Sci. Cong.*, 1931, *Chem. Sec* , Abst. 63
2.	—— and Srivastava	*Ibid.*, 1937, Abst. 23.
3.	—— and Bhargawa	*Ibid.*, 1937, Abst. 24
	—— and Narasimhan	*Ibid.*, 1939, Abst. 58.
4.	—— and Khalsa	*Ibid.*, 1937, Abst. 25
5.	—— and P. Raju	*Ibid.*, 1938, Abst. 43.
6.	Joshi	*Curr. Sci* , 1939, **8**, 548.
7.	——	Presi. Address, *Indian Sci. Cong.*, *Chem. Sec.*, 1943.
8	——	*Curr. Sci.*, 1944, **13**, 253, 278.
9.	——	*Nature*, 1944, **154**, 147.
10.	——	*Proc. Ind. Acad Sci.*, 1945, A22, 225
11.	——	*Curr. Sci* , 1945, **14**, 67.
12.	Warburg	*Z. tech. Physik*, 1923, **4**, 450 ; 1924, **5**, 165.

SIZE OF RAINDROPS

By V. N. KELKAR, M.Sc.

(Wadia College, Poona)

Received October 24, 1945
(Communicated by Diwan Bahadur Dr. K. R. Ramanathan, F.A.SC.)

THE problem of the size of raindrops is one of general meteorological interest.
It has also a bearing on visibility, sound propagation, ultra-short-wave radio
propagation, etc. In the present note the results of measurements of sizes
of raindrops deduced from the areas of splashes which they produce on pre-
pared paper are described.

The method used is briefly as follows and is on well-known lines.[1]
Drops of water of definite size are allowed to fall from different heights on
glazed paper which had been coated with ink and dried. The paper was
backed by a horizontal glass plate. On striking the paper, the drops spread
out and on drying leave a permanent record. The size of the splash increases
with the height of fall, till the critical terminal velocity is reached, after which
the size remains constant. As an example, there is shown in Fig. 1 (a) a
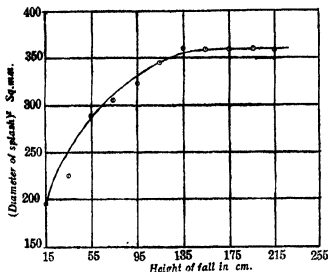
FIG. 2. Variation of size of splash with height of fall of drop

record of splashes made by drops of mass 24·8 mg. falling through heights
ranging from 15 cm. to 175 cm. Fig. 2 represents graphically the relation

394

between the area of splash and the height of fall. It is seen from the curve that after a certain height of fall, in this instance 135 cm., the area of the splash remains constant. For consistent results, it was found advantageous to absorb the excess water left as a drop on the paper by means of a piece of blotting or filter paper.

Fig. 3 shows the relation between diameter of splash and diameter of drops (assumed spherical) for drops of diameters varying from 2 mm. to 6 mm. or masses varying from 5 mg. to 110 mg. If rough paper or absorb-
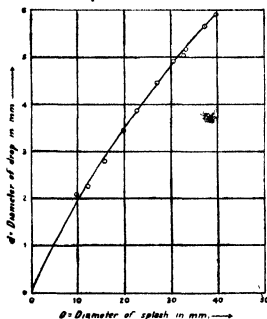
FIG. 3.

ing paper is used instead of glazed paper, it was found that the area of splash is greater and there is a greater tendency for the drop to break into smaller drops. The use of smooth paper is an innovation and a distinct improvement.

The masses of the drops were determined by collecting 200 drops in a specific gravity bottle and weighing them. It was found that for drops of masses exceeding 75 mg., a correction had to be made for the mass of the Plateau's spherule that was also weighed along with the main drop. The masses of the Plateau's spherules for various drops were determined from the areas of the splashes produced by the main drop and the Plateau's spherule. The large and the small drops were separated by subjecting them to a gentle horizontal cross-wind on their way down. If Δm represents the mass of

the Plateau's spherule and m the mass of the main drop, Fig. 4 shows the relative mass of the Plateau's spherule $\Delta\, m/m$ plotted against m. It is clear from the curve that the mass of the Plateau's spherule increases very rapidly
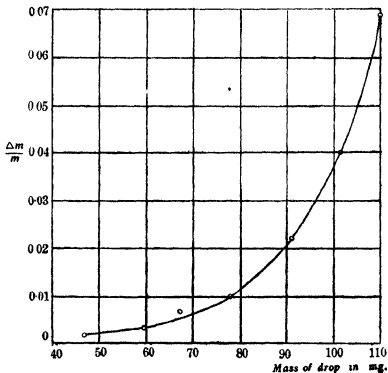
Fig 4. Variation of the Relative Mass of the Plateau's Spherule $\frac{\Delta m}{m}$ with the Mass of the Drop m

from 1% to 7% of the mass of the mother drop when m varies from 75 mg. to 110 mg. When a splash is produced by the main drop, and the Plateau's spherule lands leisurely on the splash already produced, it does not further increase the area of the splash.

The curve shown in Fig. 3 forms the basis for determining the sizes of raindrops.

Records of Raindrop Splashes.—Sheets of white paper were coated with ink and allowed to dry. Such an inked sheet was exposed to rain for a short time. On drying, a permanent record of the splashes is left on the paper. The diameters of the splashes were measured to 1/10 mm. with a millimetre scale and a magnifying glass.

A number of records were obtained for different types of showers in Poona. Some sample records are reproduced in Fig. 1 (b) and (c). Table I

TABLE I   *Percentage frequencies of diameters of raindrops*

Drizzle

Diameter (mm.) \ Date	0·0–0·5	0·5–1·0	1·0–1·5	1·5–2·0	2·0–2·5	2·5–3·0	No. of drops
8–7–1944	65·0	35·0	0·0	0·0	0·0	0·0	463
17–8–1944	53·3	45·5	1·2	0·0	0·0	0·0	940
18–8–1944	69·2	30·8	0·0	0·0	0·0	0·0	2479
Mean	62·5	37·1	0·4	0·0	0·0	0·0	3882

Light Shower

Diameter \ Date	0·0–0·5	0·5–1·0	1·0–1·5	1·5–2·0	2·0–2·5	2·5–3·0	No. of drops
7–7–1944	41·5	50·0	8·5	0·0	0·0	0·0	415
16–7–1944	6·7	43·3	34·8	15·4	0·0	0·0	200
17–7–1944	10·4	85·7	3·7	0·0	0·0	0·0	221
28–7–1944	42·2	57·8	0·0	0·0	0·0	0·0	900
18–8–1944	38·9	48·5	12·6	0·0	0·0	0·0	1394
27–9–1944	12·1	50·0	21·0	12·8	3·9	0·0	281
Mean	25·3	55·9	13·4	4·7	0·6	0·0	3211

Moderate Shower

Diameter \ Date	0·0–0·5	0·5–1·0	1·0–1·5	1·5–2·0	2·0–2·5	2·5–3·0	No. of drops
9–7–1944	2·0	27·2	64·0	6·6	0·0	0·0	180
12–7–1944	1·9	5·8	84·5	7·8	0·0	0·0	281
14–7–1944	2·1	13·4	53·5	26·8	9·7	0·0	145
16–7–1944	1·4	22·8	46·0	25·0	5·7	0·0	165
17–7–1944	0·9	41·0	53·0	0·3	0·0	0·0	230
16–8–1944	10·8	31·0	33·2	17·8	3·7	2·5	241
17–8–1944	4·6	23·0	45·0	23·9	2·7	0·0	373
21–8–1944	2·5	44·1	48·5	5·0	0·0	0·0	324
17–9–1944	18·4	22·0	34·2	25·5	0·0	0·0	381
Mean	5·0	25·8	51·3	15·4	2·4	0·3	2310

Heavy Shower

Diameter \ Date	0·0–0·5	0·5–1·0	1·0–1·5	1·5–2·0	2·0–2·5	2·5–3·0	No. of drops
11–7–1944	1·3	12·2	22·3	34·4	21·9	0·0	115
12–7–1944	0·2	4·5	36·0	45·0	13·7	0·0	95
20–7–1944	1·7	8·3	30·2	53·5	7·5	0·0	156
Mean	1·1	8·3	29·5	44·3	14·4	0·0	366

Very Heavy Shower

Diameter (mm) \ Date	0·0–0·5	0·5–1·0	1·0–1·5	1·5–2·0	2·0–2·5	2·5–3·0	3·0–3·5	3·5–4·0	4·0–4·5	4·5–5·0	5·0–5·5	No. of drops
15–9–1944	0·0	41·0	17·5	12·7	14·5	3·4	4·3	4·8	1·0	1·1	0·0	441
16–9–1944	54·5	34·5	3·7	3·2	0·9	0·7	0·8	0·6	0·5	0·6	0·2	1974
Mean	27·2	37·7	10·6	7·9	7·7	2·1	2·5	2·7	0·8	0·9	0·1	2415

shows the percentage frequencies of drops of different diameters in different showers, along with the day of observation and the number of drops for which measurements were made. Average percentages are calculated and Fig. 5 shows the average frequency polygons or histograms for drizzle, light shower, moderate shower, heavy shower and very heavy shower. These frequency polygons are plotted for intervals of diameters of $\frac{1}{2}$ mm. If smaller intervals are taken, many more peaks appear, concealing in a mass of detail the essential information that the maximum frequency corresponds to diameters between 0·0–0·5 mm. in a drizzle, between 0·5–1·0 mm. in a light shower, between 1·0–1·5 mm. in a moderate shower, between 1·5–2·0 mm. in a heavy shower and once more between 0·0–1·0 mm. in a very heavy shower, the curve however extending beyond 3 mm. diameter in the last case. The first four histograms show at a glance the progressive shifting of the mode to larger diameters as the shower gains in strength. The skewness changes from positive for light showers, through almost zero for moderate showers to negative for heavy showers.

The very heavy showers, as seen from Fig. 5 histogram, show a maximum frequency in the region of small diameters instead of large diameters, as
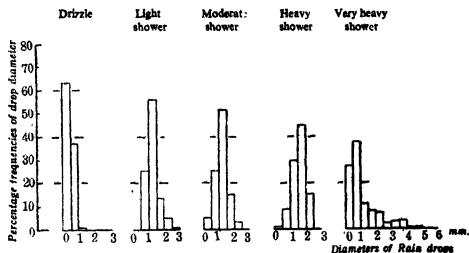
FIG 5. Percentage frequencies of diameters of rain drops in rain of different intensities

one would expect from the general trend of the preceding curves. Occasionally, when there is strongish wind near the ground, a few large drops are accompanied with a thick spray of small droplets.

Table II shows the average percentage values of the mass of water brought down by drops within different limits of diameter. Fig. 6 shows

(a)

(b)   Fig. 1   (c)
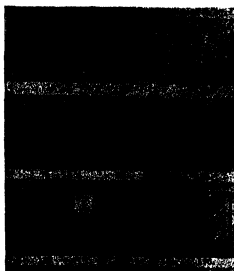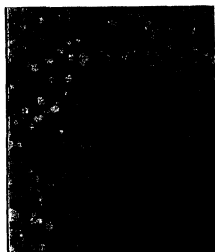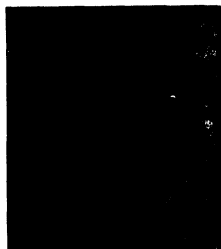
(a) Splashes caused by drops of mass 025 gm. falling through increasing heights from 15 cm. to 175 cm.

(b) and (c) Sample records of rain

TABLE II. *Average percentage precipitation in raindrops grouped according to diameters*

Nature of shower \ Diameter (mm)	0.0-0.5	0.5-1.0	1.0-1.5	1.5-2.0	2.0-2.5	2.5-3.0	3.0-3.5	3.5-4.0	4.0-4.5	4.5-5.0	5.0-5.5	No. of drops
Drizzle ..	13.8	83.0	3.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3882
Light shower	1.5	32.0	31.0	28.5	7.4	0.0	0.0	0.0	0.0	0.0	0.0	3211
Moderate shower	0.1	6.5	44.0	35.4	11.4	2.6	0.0	0.0	0.0	0.0	0.0	2310
Heavy shower	0.0	0.9	13.1	51.0	35.0	0.0	0.0	0.0	0.0	0.0	0.0	366
Very heavy shower	0.2	3.2	3.7	7.2	14.5	7.2	14.2	23.0	10.0	14.5	2.0	2415
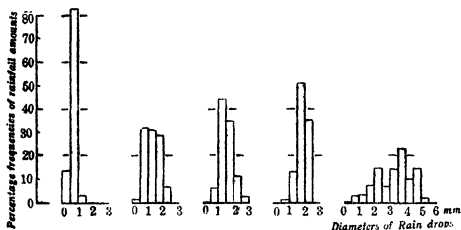
FIG. 6. Percentage frequencies of rainfall amounts carried down by drops of different sizes.

the results plotted graphically. Figs. 5 and 6 together convey the complete information regarding the distribution of size frequency and the amount of rainfall brought down by drops of different sizes.

The method described is competent to measure (1) the intensity of precipitation in very short time intervals, (2) the number of drops per cubic metre of air in a shower together with the size distribution and (3) the distribution of drop size from different part of a rain cloud.

The author is thankful to Diwan Bahadur Dr. K. R. Ramanathan for encouragement and useful suggestios.

REFERENCE

¹ The method of using a filter paper was originally due to J Wiesner and was improved by P. Lenard and A. Defant. For references, please see " Handbuch der Meteorologischen Instrumente " by E. Kleinschmidt, *J. Springer*, 1935, p. 273

CONDENSATION OF ALDEHYDES WITH MALONIC ACID

Part XVI. With p- and m-Methylbenzaldehydes: p- and m-Methyl-benzylidenemalonic Acids

By Prem Narain Agarval, Kantilal C. Pandya and Indra Lal Tripath

(Chemistry Laboratory, St. John's College, Agra)

In this paper the influence of a methyl group on the aromatic ring of the aldehyde, in the aldehyde-malonic acid condensation, is investigated. The influence of such a methyl group on the yields in the Perkin's reaction has been reported by Lock and Bayer[1] under standard conditions to be as under:

Position of the Me group	o	m	p	2-4-6
% Yield ..	15	33	15	0·6

as compared with 49% from the unsubstituted benzaldehyde. The depressing effect of the methyl group is very clearly shown. By increasing the heating time of the 2-4-6-tri-methylbenzaldehyde, from eight to fifty hours, the authors were able to raise up the yield from 0·5 to only 8%.

The first study of this in the aldehyde-malonic acid condensation, using pyridine in traces was made by Kurien and Pandya[2] (1934) who obtained 84% of p-methylcinnamic acid from p-tolylaldehyde. Later Mehra and Pandya[3] (1936) obtained, on five hours' heating, 93% yield of the same product. In the present paper about 98% yield is reported, suggesting, therefore, that in the condensation by this method, the methyl group in the p-position did not depress, but possibly increased, the yield. On heating the p-tolylaldehyde alone with malonic acid on the water-bath for five hours, p-tolylidenemalonic acid, melting at 201° came out in 75% yield No doubt longer heating might have increased the yield though decarboxylation also might have occurred. Heating the aldehyde and the acid with glacial acetic acid, following Stuart,[4] gave only about 30% of the dibasic acid. The mono- and the dibasic acids had their melting-points very near, but the dibasic acid melted always with effervescence as one would expect. It was further confirmed by titration with standard alkali and by the silver salt, as well as by a mixed melting-point with the mono- or cinnamic acid.

In the condensation of the *m*-tolylaldehyde a peculiarity made its appearance which tended very greatly to restrict the yield of the pure product, though there was enough evidence to show that the condensation otherwise went very well. This peculiarity was that under the ordinary method of conducting the condensation with a trace of pyridine, the condensation product that came out was always a mixture of the mono- and the dibasic acids. It came out in good yields but it always melted from 92° to about 143°. About a dozen experiments with changes in the conditions of heating were made but they failed to secure only one pure product, though the proportions of the two among themselves varied. Separation of the two by means of solvents did not succeed. Increase of pyridine from 0·15 mol. to about 6 mols., with corresponding changes in the temperature and hours of heating gave the mono, the *m*-methylcinnamic acid, melting at 113–14°. The yield however was about 68%, probably on account of insufficient heating (*vide* Tables). Further increase took place when heating was abandoned and long time at room-temperature was given: thus by following the method of Vorsatz,[5] an almost quantitative yield of the *m*-methyl-cinnamic acid was obtained. (The acid had been prepared by means of the Perkin's reaction by Bornemann[6] and by Müller[7]. Lock and Bayer[1] also obtained it later. The first two do not mention yield.)

The *m*-methylbenzylidenemalonic acid does not seem to be mentioned in literature and is prepared for the first time. It was obtained here in a pure condition by the usual method of heating the aldehyde and the malonic acid alone on water-bath for six hours when about 30% yield was obtained. Stuart's method of using glacial acetic acid increased the yield to about 48%.

Condensation of p-Tolylaldehyde in the presence of Glacial Acetic Acid.— 1·2 g. *p*-tolylaldehyde, 1 g. malonic acid and 3 c.c. glacial acetic acid, heated on the water-bath for five hours, gave 0·6 g. of the *p*-tolylidenemalonic acid, *i.e.*, about 30%. The acid melted at 201°, was insoluble in cold, but soluble in hot water; it melted with effervescence, showed unsaturation and was soluble in ether, benzene and glacial acetic acid. Equivalent weight, by titration = 104·3, by silver salt = 105. $C_{11}H_{10}O_4$ requires 103.

*Condensation in the absence of any Condensing Reagent.—*The aldehyde and the acid were heated for two hours on water-bath and thereafter in an oil-bath, 110–120°, for 2·5 hours. The product was taken out as usual and weighed 1·5 g. (= 75% yield).

Condensation with a trace of Pyridine (1 : 1 : 0.·2 mol.).—The aldehyde, the acid and pyridine, taken as above, were heated (compare Mehra and

Pandya[3]) as usual: about 98% yield was obtained. The p-methylcinnamic acid melting at 195° (pure m.p. 197-98°), when mixed with the dibasic p-tolylidenemalonic acid, m.p. 201°, melted at 180°.

Condensation of m-Tolylaldehyde, in the presence of Pyridine.—The[3] table gives the details. Aldehyde taken was 1·2 g.

Condensing Agent	Proportion mol.	Temperature	Time hrs.	Product m.p.	Yield
Pyridine	0·15	Waterbath	5	98-139°	
,,	,,	,,	8	98-140°	
,,	,,	,,	12	,,	
,,	,,	100-105°	18	98-143°	
,,	,,	,,	5	,,	
,,	,,	,,	10	,,	
,,	,,	,,	16	,,	
,,	0·2	105-110°	17	95-139°	
,,	0·5	Waterbath	6·5	96-133°	1·65 g.
,,	,,	,,	6		
,,	1	Then 110-115°	8	98-141°	
,,	2	110-115°	18	94-139°	
,,	3	115-120°	17	95-143°	
The mixture of the acids was heated with pyridine, 1·0 g. with					
,,	0·3	Waterbath	2		
,,		Then 110-120°	2	98-143°	
,,	3·0	as above	4		
,,	3	Refluxed over wire-gauze	2	110-111°	60%

This product on recrystallization (alcohol and ligroin) melted at 113-114°, which remained constant after further crystallisation. The yield was over 60%. Its properties coincided with those described by Heilbron. Oxidation with potassium permanganate gave m-toluic acid, m.p. 110-111°. Bromine water gave an acid, dibrom derivative, m.p. 164-67°.

The cinnamic acid was also obtained pure when the aldehyde, the acid and pyridine in 1:1:4 mol. proportion were heated on waterbath for 2·5 hours and then refluxed on wire-gauze for half an hour. Yield = 62%. m.p. 114°.

Long time and room temperature condensations were also tried. The best yield was nearly quantitative yield obtained by the application of Vorsatz's method of keeping the aldehyde and the acid in a flask with about 6 mols. of pyridine and a few drops of piperidine for three months.

Condensation in the Absence of Pyridine: m-Tolylidenemalonic Acid.— The aldehyde and malonic acid were heated alone on waterbath for varying periods: the product in the crude form melted between 160-68° and, after recrystallization, at 172-74° with effervescence. The yield varied, according

to the heating time, from 20 to 32%. Less than five hours' heating gave little sign of the condensation having occurred, while longer heating or higher temperature produced the mixture of the di- and the mono-acids referred to above.

Condensation in the presence of Glacial Acetic Acid.—The aldehyde, malonic acid and glacial acetic acid (1 : 1 : 3 mol.), were heated on water-bath for about six hours, the dibasic acid was obtained, m.p. 172°, in 48% yield. The dibasic acid *m*-tolylidenemalonic acid was soluble in alcohol. Repeated recrystallisations from benzene-alcohol mixture raised the melting point to 173–74°, effervescence always accompanying the melting. It was also soluble in ether, chloroform and ethyl acetate: it was almost insoluble in cold water, benzene and glacial acetic acid. It readily decolourised in the cold Baeyer's reagent, and also bromine water. Rast's method of determining the molecular weight was not applicable as it decomposed on melting with camphor. Equivalent weight found by alkaline titration was = 103·9, the acid $C_{11}H_{10}O_4$ requires 103. The molecular weight by the silver salt method was 206·7 : required 206.

TABLE

The influence of the methyl group on the yield

	Benzaldehyde	Position of Me group		
		o	*m*	*p*
By Perkin's Reaction	49%	15	33	15
„ Pyridine Trace ..	95	..	68	98
„ Voratz's Method	..	..	..	98

SUMMARY

The condensation of *p*-tolylaldehyde with malonic acid by the pyridine-trace method gave, on repetition, a nearly quantitative yield of the *p*-tolylidene-acrylic (*p*-methylcinnamic) acid. *p*-Tolylidenemalonic acid has been isolated for the first time in this condensation, in the absence of pyridine, in 75% yield.

m-Tolylaldehyde, on condensation with malonic acid in the presence of pyridine in traces, gave up to 68% of the *m*-methylcinnamic acid. By a long-time-room-temperature condensation in the presence of both pyridine and piperidine, the yield came up to the theoretical. The *m*-tolylidenemalonic acid came out best in the presence of glacial acetic acid, but the yield was not great, being = 48%.

REFERENCES

1. Lock and Bayer   *Ber.*, 1939, **72**, 1064.
   Böck, Lock and Schmidt   *Monat.*, 1934, **64**, 399
2. Kurien and Pandya   *J. I. C. S.*, 1934, **11**, 825.
3. Mehra and Pandya   *Proc. Ind. Acad. Sci.*, A, 1936, **6**, 510.
4. Stuart   . *J C. S.*, 1883, **53**, 142.
5. Vorsatz   *J prakt. Chem.*, 1936, **145**, 265
6. Bornemann   . *Ber* , 1884, **17**, 1462, 1476
   Müller   *Ibid.*, 1887, **20**, 1212
   Heilbron   *Dictionary of Organic Chemistry.*

A METHOD OF PREPARING DIFFUSING SCREENS OF DEFINITE NEBULOSITIES FOR VISIBILITY METERS

By C. S. KARVE, M.Sc., PH.D.

(Department of Physics, S P College, Poona)

THE most important factor which determines the maximum distance of objects which can be seen and distinguished under natural conditions is the scattering and absorbing power of the suspended matter in the atmosphere. In the two most common visibility-meters in general use, those of Wigand and Bennett, the visibility of an object is generally determined by interposing a diffusing screen of such nebulosity in front of the eye that the object is just indistinguishable from the background. In the course of a critical examination of these instruments it was found that a common defect of these instruments was the variability of the diffusing screens used in them and their want of standardisation. In order to make a reproducible visibility meter, it was considered necessary to develop a method of preparing standardised diffusing screens of different nebulosities. The present note describes briefly the method that was worked out to achieve this.

In brief, the method consists in coating a glass plate with a definite thickness of a gelatine emulsion containing a uniform fine-grained white precipitate of barium sulphate in suspension. The nebulosity of the screen can be varied within limits by varying the concentration or the thickness of the emulsion. At first, the attempt was made to produce the precipitate in the gelatine of commercial photographic plates from which the silver salts had been removed, but as the plates usually available in the Indian market are hardened, the precipitate could not be formed in them in a uniform and reproducible manner.

The method of preparing the emulsions and coating the glass plates ally adopted is as follows: —

The following three solutions were prepared: —

(1) Gelatine	.	.	5 gm. in 100 c.c. of water.
(2) BaCl₂	..	..	2·44 gm.	do.
(3) Potash Alum	..	..	9·5 gm.	do.

405

The gelatine used was of French Gold Label quality and had a pH value of 5·8 to 6·0. The Barium Chloride solution was added to the gelatine solution in a beaker and after thorough stirring with a glass stirrer, the mixture was kept at a constant temperature of 35° C. An approximately equivalent quantity of alum solution was quickly added and the mixture again well stirred for another three minutes. A definite quantity of this Barium Sulphate emulsion was then poured on a chemically clean glass plate kept perfectly level and distributed uniformly over the plate by means of a clean glass rod The plate was immediately placed in a chamber maintained at 16° to 18° C. After the emulsion had set, it was dried in a dust-free chamber at a temperature not exceeding 20° C.

To make reproducible screens, it is important to keep the temperature at which the emulsion is formed nearly the same and mix the alum solution in the same manner (e.g., in one lot) to the Barium Chloride solution.

It was found that for a definite strength of the gelatine solution, there is an upper limit to the amount of Barium Sulphate that can be held in colloidal form and beyond this limit the particles become too large. For a 5 per cent. solution of gelatine, the maximum amount of $BaSO_4$ was about ·002 gm. per c.c. With a stronger solution of gelatine the mixture became too viscous to spread uniformly over the plate.

Plates prepared in the above manner with 20 c.c. of emulsion spread over a cabinate size plate were found to have the following values of transparency when measured with a Lummer-Brodhun Photometer.

TABLE I

$BaSO_4$ spread per sq. cm.	Transparency per cent.
8·1 × 10⁻⁶ gm.	82·0
12·8 × 10⁻⁶ gm.	75·8
21·0 × 10⁻⁶ gm.	67·0

To get greater opacities, filters can be combined in series.

The lowest limit of transparency in this method happens to be earlier due to the hardening action of potash alum on the $BaSO_4$ grain. In order to remove this defect similar plates were also prepared by preparing $BaSO_4$ emulsion by the action of Sodium Sulphate on Barium Chloride. Following strengths of different constituents were used.

    (1) Gelatine   .. 10 gm. dissolved in 100 c.c.
    (2) $BaCl_2$ .. 2·44 gm.   do.
    (3) Na_2SO_4 .. 1·42 gm.   do.

The emulsion was always prepared at 35° C. The transparencies obtained for different concentrations are given in Table II

<div align="center">TABLE II</div>

BaSO₄ spread per sq. cm.	Transparency per cent
2·1 × 10⁻⁴ gm.	72·8
4·2 × 10⁻⁴ gm.	65·8
8·4 × 10⁻⁴ gm.	57·0
12·6 × 10⁻⁴ gm.	48·8
16·8 × 10⁻⁴ gm.	40·7

Although the lowest limit of transparency which is 41 per cent. in this method can be extended further by using gelatine solution of higher strength still it is not safe to do so. The reason is that such a solution has to be prepared at about 50° C. and it is found that the transparency of the plates changes rapidly when the emulsion is prepared between 40° C. and 60° C.

I have to thank Dr. K. R. Ramanathan, M.A., D.Sc., for the suggestion of the problem and his interest in the work. My warmest thanks are due to my friend Dr. J. V. Karandikar, M.Sc., Dr. Eng. (Berlin), for his useful technical suggestions in preparing the diffusing screens. Lastly, I must also record my thanks to Principal G. R. Paranjpe, Royal Institute of Science, Bombay, for kindly allowing me the facilities of the Photographic Laboratory of his Institute.

<div align="center">SUMMARY</div>

A new method of preparing diffusing screens of different nebulosities by coating good glass plates by an emulsion of Barium Sulphate formed in gelatine, is described. The BaSO₄ emulsion is prepared in two ways. In the first method BaCl₂ and potash alum are used while in the second, BaCl₂ and Na₂SO₄ are used. In the former process the lowest limit of transparency is soon reached while in the other it can be extended further. The transparency of these screens is measured with a Lummer-Brodhun Photometer. The results of the measurements show that the screens obtained by this process are reproducible and follow the law of additivity.

A5

PAULI'S IDENTITIES IN THE DIRAC ALGEBRA

BY B. S. MADHAVA RAO, F.A.Sc.

(Department of Mathematics, Central College, Bangalore)

1. INTRODUCTION

DIRAC matrices are defined by the relations

$$\tfrac{1}{2} \left(\gamma^\mu \gamma^\nu + \gamma^\nu \gamma^\mu \right) = \delta_{\mu\nu} \tag{1}$$

$$(\delta_{\mu\nu} = 0 \text{ for } \mu \neq \nu, \ \delta_{\mu\mu} = 1; \ \mu, \ \nu = 1, 2, 3, 4)$$

and as is well known the 16 elements 1, γ^μ, $i\gamma^\mu\gamma^\nu$ ($\mu \neq \nu$), $i\gamma^\lambda\gamma^\mu\gamma^\nu$ (λ, μ, ν different), and $\gamma^1\gamma^2\gamma^3\gamma^4$ form a system of hypercomplex numbers constituting the Dirac algebra Following Pauli (1936) we will write the above elements in the form*

$$1, \ \gamma^\mu, \ \gamma^{[\mu\nu]}, \ \gamma^{[\lambda\mu\nu]}, \ \gamma^5 \tag{2}$$

the square brackets indicating anti-symmetry in the indices, and denote any one of the sixteen elements as γ^A (the latin index A runs through from 1 to 16). The factors i are included in the definition of the $\gamma^{[\mu\nu]}$ and $\gamma^{[\lambda\mu\nu]}$, and are so chosen that for every A, $(\gamma^A)^2 = 1$. The product of any two elements γ^A and γ^B is always equal to a third element γ^C except for a numerical factor which has one of the values ± 1, $\pm i$. The γ^A have thus the group property and the introduction of the co-efficients -1, $\pm i$ in the multiplication table makes the group of the symbols γ^A one of order 64. This group can be shown to have two representations of degree four and thirty-two of degree one. Any finite group can be associated with an algebra (the Frobenius algebra) such that the algebra of the group is the direct sum of the algebras of its representations as groups of linear substitutions. For the group of order 64, it can be shown (D E. Littlewood, 1934) that the group algebra can be reduced to one single matrix algebra of degree four associated with the γ^A, viz., the Dirac algebra.

The Dirac matrices γ^μ permit the relativistic wave equation of the electron being written in the form

$$\gamma^\mu \partial\psi / \partial x^\mu + \kappa\psi = 0, \tag{3}$$

where γ^μ and ψ are 4×4 and 4×1 matrices respectively, and $\kappa = mc/\hbar$. The Lorentz invariance of (3) can be proved by establishing the existence of a

---

* We follow in this paper the notation of that of Pauli (1936) which will be referred to hereafter as P.

matrix Λ specifying the transformation $\psi' - \psi$ of $\Lambda\psi$ under a Lorentz transformation. With the aid of (3) and a function $\psi^\dagger$ (a 1×4 matrix) satisfying the wave equation

$$\frac{\partial \psi^\dagger}{\partial x^\mu} \gamma^\mu - \kappa \psi^\dagger = 0 \tag{3\dagger}$$

and transforming according to $\psi^{\dagger\prime} = \psi^\dagger \Lambda^{-1}$, one can construct the following co-variants:

$$
\left.
\begin{aligned}
\text{the invariant} && \psi^\dagger \psi &= i\Omega_1 \\
\text{the vector} && \psi^\dagger \gamma^\mu \psi &= S_\mu \\
\text{the antisymmetric tensor} && \psi^\dagger \gamma^{[\mu\nu]} \psi &= -i \, M_{[\mu\nu]} \\
\text{the pseudo-vector} && \psi^\dagger \gamma^{[\lambda\mu\nu]} \psi &= S_{\lambda\mu\nu} \\
\text{\& the pseudo-scalar} && \psi^\dagger \gamma \psi &= \Omega_2
\end{aligned}
\right\} \tag{4}
$$

Between these co-variants Ω_1, Ω_2, S_μ, $M_{[\mu\nu]}$ and $S_{[\lambda\mu\nu]}$ there exist certain quadratic identities (P. 131), *viz.*

$$
\left.
\begin{aligned}
& -\sum_\mu S_\mu^2 = \Omega_1^2 + \Omega_2^2 \\
& \sum_{[\mu\nu]} M_{[\mu\nu]}^2 = \Omega_1^2 - \Omega_2^2 \\
& -\sum_{[\lambda\mu\nu]} S_{[\lambda\mu\nu]}^2 = \Omega_1^2 + \Omega_2^2 \\
& -\frac{i}{2} \sum_{[\chi\lambda],\,[\mu\nu]} M_{[\chi\lambda]} \, M_{[\mu\nu]} = \Omega_1 \, \Omega_2 \\
& \sum_{\chi,\,[\lambda\mu\nu]} S_\chi \, S_{[\lambda\mu\nu]} = 0
\end{aligned}
\right\} \tag{5, a to e}
$$

where the indices $\chi\lambda\mu\nu$ are different from one another

These identities have been established by Pauli (P. 131–36) in a general manner without making use of any particular representation of the γ^μ and also taking ψ & $\psi^\dagger$ to be entirely arbitrary one-column and one-row matrices of degree four. The proof consists in generalising the quadratic identities to those bilinear in pairs $(\phi, \phi^\dagger)$, and $(\psi, \psi^\dagger)$ of such matrices and putting $\phi \cdot \psi$, $\phi^\dagger = \psi^\dagger$ in these generalized identities. This method has however been applied to derive (5, b), (5, d), and [(5, a) + (5, c)] while (5, a), and (5, e) are obtained directly without the introduction of a second pair $(\phi, \phi^\dagger)$, and by using the properties of the B-matrix (P. 121).

We give here a simple method of deriving identities generalising (5). This method consists in taking products of the γ^A with 4×4 matrices of rank unity (*i.e.*, matrices expressed as the product of a one column and a one-row

matrix) and expressing these products as linear combinations of the elements of the basis of the algebra by using the commutation rules (1). We showed that by suitably choosing these products it is possible to derive not only bilinear identities of the Pauli type, but other 'tensor', multi-linear, and polynomial identities. It is also shown that, in general, products of the five types

$$\psi\psi^\dagger, \quad \gamma^\mu\psi\psi^\dagger, \quad \gamma^{[\mu\nu]}\psi\psi^\dagger, \quad \gamma^{[\lambda\mu\nu]}\psi\psi^\dagger, \quad \gamma^5\psi\psi^\dagger \qquad (2,\,a)$$

are sufficient to obtain all possible identities.

Similar results have recently been obtained by Harish-Chandra (1945) by using Eddington's E-numbers. It is clear that the abstract algebra of these E-numbers is the algebra of matrices of degree four, the difference being merely a change of basis of the algebra, and it is doubtful if the change of basis from the γ^A to the E-numbers really leads to any simplification in the algebraic work. Our results show that the identities in question do not depend on any particular choice of the basis of the algebra, but are consequences of expressing particular types of matrices in terms of the basis elements.

2. METHOD OF DERIVATION OF IDENTITIES

Since γ^A constitute a basis of the complete matric Dirac algebra any arbitrary matrix of the fourth degree T can be represented in the from

$$T = \sum_A t_A \gamma^A \qquad (6)$$

by suitably choosing the numbers t_A. Also the spur of each γ^A is zero except $\gamma^A = 1$ (P. 112, lemma 5), i.e

$$\text{Spur } \gamma^A = 0, \quad \gamma^A \neq 1. \qquad (7)$$

Multiplying both sides of (6) by a particular γ^A and taking spurs we get

$$\text{Sp } (\gamma^A \, T) = 4 \, t_A \qquad (8)$$

and we can write (6) as

$$4 \, T = \sum_A \text{Sp } (\gamma^A \, T) \, \gamma^A = \sum \text{Sp } (T \, \gamma^A) \, \gamma^A \qquad (9)$$

Let $\psi, \phi, \chi.$. be one-column, and $\psi\dagger, \phi^\dagger, \chi^\dagger, \ldots\ldots$ one-row matrices of degree four respectively. For purposes of derivation of the identities in question the ψ and $\phi^\dagger$, etc., may be entirely arbitrary and independent and not necessarily related as solutions of the wave equation (3) and its adjoint ($3^\dagger$). From these we form 4×4 matrices of the type $\psi\phi^\dagger, \psi\phi^\dagger$ etc. The importance of such types arises from the fact that these matrices are of rank unity, and this property is known to be independent of the representation of the algebra but is a property of the abstract algebra itself. We next choose a matrix T as the product of these matrices of rank unity with fixed elements γ^B, γ', etc.,

substitute in (9), and multiply both sides of (9) by a $\psi^\dagger$ on the left and a ψ on the right. By evaluation of the spurs on the right-hand side of (9) using the commutation rules (1), the above process gives rise to an identity of the type under consideration. For example, if we take

$$\mathbf{T} = \gamma^\mu \ \psi\psi^\dagger \qquad (\mu \text{ fixed})$$

the process outlined above gives

$$\left.\begin{array}{l} 4\,(\psi^\dagger\gamma^\mu\psi)\,(\psi^\dagger\psi) = \underset{\Lambda}{\Sigma}\,\mathrm{Sp}\,(\gamma^\mu\psi\psi^\dagger\gamma^\Lambda)\,(\psi^\dagger\gamma^\Lambda\psi) \\[2mm] \text{or, } 4\,(\phi^\dagger\gamma^\mu\chi)\,(\psi^\dagger\phi) = \underset{\Lambda}{\Sigma}\,\mathrm{Sp}\,(\gamma^\mu\psi\psi^\dagger\gamma^\Lambda)\,\phi^\dagger\gamma^\Lambda\phi) \end{array}\right\} \qquad (10,\,a,\,b)$$

according as we multiply by $\psi^\dagger$ on the left and ψ on the right, or $\phi^\dagger$ on the left and ϕ on the right. The spur expression on the right of (10, a) or (10, b) is equal to

$$\mathrm{Sp}\,(\psi^\dagger\gamma^\Lambda\gamma^\mu\psi) = (\psi^\dagger\gamma^\Lambda\gamma^\mu\psi)$$

since the product inside the bracket is a 1×1 matrix We can easily evaluate the several $\gamma^\Lambda\gamma^\mu$ using the rules (1), and obtain a quadratic identity from (10, a) and a bilinear one from (10, b) Alternatively we might take $\mathbf{T} = \gamma^\mu \ \psi \ \phi^\dagger$ and use the prescription of multiplying on the left by $\psi^\dagger$, and on the right by ϕ. This gives another bilinear identity The same considerations can be easily extended to more than two matrices

3 BILINEAR AND QUADRATIC IDENTITIES

The elements of the basis of the algebra can be grouped into the five types given by (2). Of these the fourth type can be written as $\hat\gamma^\kappa$ dual to γ^κ defined in the usual manner (P. 132), and the elements classified as

$$1,\ \gamma^\mu,\ \gamma^{[\mu\nu]},\ \hat\gamma^\mu,\ \hat\gamma^5 \qquad\qquad (2,\,b)$$

For purposes of deriving the bilinear identities involving ϕ & ψ, and thereby deducing the quadratic ones by putting $\phi = \psi$ & $\phi^\dagger = \psi^\dagger$, we consider products of the type $\gamma^B\gamma^A\gamma^B$, and keeping A fixed we sum for the index B over the elements in the several types (2, b) We then vary the index A itself to refer successively to any one element in each of these types. The several sums that arise thus can be evaluated by using (1). For example,

$$\underset{\mu}{\Sigma}\,(\gamma^\mu\gamma^\Lambda\gamma^\mu) = 4, -2\gamma^\nu,\ 0,\ 2\hat\gamma^\nu,\ \text{or } -4\gamma^5$$

according as $\gamma^\Lambda = 1,\ \gamma^\nu,\ \gamma^{[\lambda\nu]},\ \hat\gamma^\nu$ or $\hat\gamma^5$ respectively as can be easily verified. We tabulate below the sums obtained by following the above procedure. This table can be used for deriving the bilinear identities, and can be considered a generalisation of lemma 6 of Pauli's paper (P. 113).

TABLE OF SUMS $\sum\limits_{B} \gamma^B \gamma^A \gamma^B$

$\gamma^A =$ Sums	1	γ^μ	$\gamma^{[\mu\nu]}$	$\hat\gamma^\mu$	γ^5
$1 \; \gamma^A . 1$	1	γ^μ	$\gamma^{[\mu\nu]}$	$\hat\gamma^\mu$	γ^5
$\sum \gamma^\mu \gamma^A \gamma^\mu$	4	$-2\gamma^\mu$	0	$2\hat\gamma^\mu$	$-4\gamma^5$
$\sum \gamma^\mu \gamma^A \hat\gamma^\mu$	$4i\gamma_5$	$-2\hat\gamma^\mu$	0	$-2\gamma^\mu$	$-4i$
$\sum \hat\gamma^\mu \gamma^A \gamma^\mu$	$-4i\gamma^5$	$2\hat\gamma^\mu$	0	$-2\gamma^\mu$	$4i$
$\sum \hat\gamma^\mu \gamma^A \hat\gamma^\mu$	4	$2\gamma^\mu$	0	$-2\hat\gamma^\mu$	$-4\gamma^5$
$\sum \gamma^{[\mu\nu]} \gamma^A \gamma^{[\mu\nu]}$ $= \sum \hat\gamma^{[\mu\nu]} \gamma^A \hat\gamma^{[\mu\nu]}$	6	0	$-2\gamma^{[\mu\nu]}$	0	$6\gamma^5$
$\sum \gamma^{[\mu\nu]} \gamma^A \hat\gamma^{[\mu\nu]}$ $= \sum \hat\gamma^{[\mu\nu]} \gamma^A \gamma^{[\mu\nu]}$	$-6\gamma^5$	0	$-2\hat\gamma^{[\mu\nu]}$	0	-6
$\gamma^5 \gamma^A \gamma^5$	1	$-\gamma^\mu$	$\gamma^{[\mu\nu]}$	$-\hat\gamma^\mu$	γ^5

$$(11)$$

We now take $T = \sum\limits_{B} \gamma^B \phi \phi^\dagger \gamma^B$ or $T = \sum\limits_{B} \gamma^B \phi \phi^\dagger \gamma^B$, and apply the procedure outlined in the previous article. The summations over B for the several types of γ^A are taken from the rows of table (11), and the above two expressions for T yield in all 16 identities which we will now write down. In doing so we shall use the tensors dual to $M_{[\mu\nu]}$ and $S_{(\lambda\mu\nu)}$, $viz.$ $\hat{M}_{[\mu\nu]} \equiv M_{[\mu\nu]}$ and $\hat{S}_x \equiv S_{(\lambda\mu\nu)}$, and also indicate by dashes the convariants defined with respect to ϕ & $\phi^\dagger$.

(1) $T = \psi\psi^\dagger$, and $T = \phi\phi^\dagger$ lead respectively [by using the first row of (11)] to :

$$- 4 \; \Omega_1\Omega_1' = (\phi^\dagger\psi)\,(\psi^\dagger\phi) + \sum (\psi^\dagger\gamma^\mu\phi)\,(\phi^\dagger\gamma^\mu\phi) + \sum (\psi^\dagger\gamma^{[\mu\nu]}\psi)\,(\phi^\dagger\gamma^{[\mu\nu]}\phi)$$
$$+ \sum (\phi^\dagger\hat\gamma^\mu\psi)\,(\psi^\dagger\hat\gamma^\mu\phi) + (\phi^\dagger\gamma^5\psi)\,(\psi^\dagger\gamma^5\phi) \tag{12, a}$$

$$4\,(\psi^\dagger\psi)\,(\phi^\dagger\psi) = - \; \Omega_1\Omega_1' + \sum S_\mu S_\mu' - \sum M_{[\mu\nu]}\,M'_{[\mu\nu]}$$
$$+ \sum S_\mu \, \hat{S}' + \Omega_5\Omega_5' \tag{12, b}$$

Putting $\phi = \psi$; $\phi^\dagger = \psi^\dagger$ both these lead to

$$3\,\Omega_1^2 + \Omega_2^2 = \Sigma\,\mathsf{S}_\mu^2 + \Sigma\,\mathsf{M}_{[\mu\nu]}^2 - \Sigma\,\hat{\mathsf{S}}_\mu^2 \qquad (12, c)$$

(2) $\mathbf{T} = \Sigma\,\gamma^\mu\psi\phi^\dagger\gamma^\mu$, and $\mathbf{T} = \Sigma\,\gamma^\mu\phi\phi^\dagger\gamma^\mu$ [using second row of (11)]·

$$4\,\Sigma\,\mathsf{S}_\mu\mathsf{S}_\mu' = 4\,(\phi^\dagger\psi)\,(\psi^\dagger\phi) - 2\,\Sigma\,(\phi^\dagger\gamma^\mu\psi)\,(\psi^\dagger\gamma^\mu\phi)$$
$$+ 2\,\Sigma\,(\phi^\dagger\gamma^\mu\psi)\,(\psi^\dagger\gamma^\mu\phi) - 4\,(\phi^\dagger\gamma^5\psi)\,(\psi^\dagger\gamma^5\phi) \quad (13, a)$$

$$4\,\Sigma\,(\psi^\dagger\gamma^\mu\psi)\,(\phi^\dagger\gamma^\mu\phi) = -\,4\,\Omega_1\Omega_1' - 2\,\Sigma\,\mathsf{S}_\mu\mathsf{S}_\mu' + 2\,\Sigma\,\hat{\mathsf{S}}_\mu\hat{\mathsf{S}}_\mu' - 4\,\Omega_2\Omega_2' \quad (13, c)$$

Both these lead to

$$3\,\Sigma\,\mathsf{S}_\mu^2 - \Sigma\,\hat{\mathsf{S}}_\mu^2 = -\,2\Omega_1^2 - 2\Omega_2^2 \qquad (13, c)$$

(3) $\mathbf{T} = \Sigma\,\gamma^\mu\psi\phi^\dagger\gamma^\mu$, and $\mathbf{T} = \Sigma\,\gamma^\mu\phi\phi^\dagger\gamma^\mu$ [using fourth row of (11)].

$$4\,\Sigma\,\mathsf{S}_\mu\hat{\mathsf{S}}_\mu' = -\,4i\,(\phi^\dagger\gamma^5\psi)\,(\psi^\dagger\phi) - 2\,\Sigma\,(\phi^\dagger\hat{\gamma}^\mu\psi)\,(\psi^\dagger\gamma^\mu\phi)$$
$$-\,2\,\Sigma\,(\phi^\dagger\gamma^\mu\psi)\,(\psi^\dagger\hat{\gamma}^\mu\phi) + 4i\,(\phi^\dagger\psi)\,(\psi^\dagger\gamma^5\phi) \qquad (14, a)$$

$$4\,\ldots(\psi^\dagger\gamma^\mu\psi)\,(\phi^\dagger\hat{\gamma}^\mu\phi) = 4\,\Omega_1\Omega_2' - 2\,\Sigma\,\mathsf{S}_\mu\hat{\mathsf{S}}_\mu' - 2\,\Sigma\,\hat{\mathsf{S}}_\mu\mathsf{S}_\mu' - 4\,\Omega_2\Omega_1' \quad (14, b)$$

Both these lead to

$$\Sigma\,\mathsf{S}_\mu\hat{\mathsf{S}}_\mu = 0 \qquad (5, e) \text{ or } (14, c)$$

(4) $\mathbf{T} = \Sigma\,\hat{\gamma}^\mu\psi\phi^\dagger\gamma^\mu$, and $\mathbf{T} = \Sigma\,\hat{\gamma}^\mu\phi\phi^\dagger\gamma^\mu$ [using third row of (11)]·

$$4\,\Sigma\,\hat{\mathsf{S}}_\mu\mathsf{S}_\mu' = 4i\,(\phi^\dagger\gamma^5\psi)\,(\psi^\dagger\phi) - 2\,\Sigma\,(\phi^\dagger\hat{\gamma}^\mu\psi)\,(\psi^\dagger\gamma^\mu\phi)$$
$$-\,2\,\Sigma\,(\phi^\dagger\lambda^\mu\psi)\,(\psi^\dagger\hat{\gamma}^\mu\phi) - 4i\,(\phi^\dagger\psi)\,(\psi^\dagger\gamma^5\phi) \qquad (15, a)$$

$$4\,\Sigma\,(\psi^\dagger\gamma^\mu\psi)\,(\phi^\dagger\gamma^\mu\phi) = -\,4\,\Omega_1\Omega_2' + 2\,\Sigma\,\mathsf{S}_\mu\hat{\mathsf{S}}_\mu' - 2\,\Sigma\,\mathsf{S}_\mu\mathsf{S}_\mu' + 4\,\Omega_2\Omega_1' \quad (15, b)$$

Both these lead to

$$\Sigma\,\hat{\mathsf{S}}_\mu\mathsf{S}_\mu = 0. \qquad (5, e) \text{ or } (15, c)$$

(5) $\mathbf{T} = \Sigma\,\hat{\gamma}^\mu\psi\phi^\dagger\gamma^\mu$, and $\mathbf{T} = \Sigma\,\hat{\gamma}^\mu\phi\phi^\dagger\gamma^\mu$ [using fifth row of (11)]·

$$4\,\Sigma\,\hat{\mathsf{S}}_\mu\hat{\mathsf{S}}_\mu' = 4\,(\phi^\dagger\psi)\,(\psi^\dagger\phi) + 2\,\Sigma\,(\phi^\dagger\gamma^\mu\psi)\,(\psi^\dagger\gamma^\mu\phi) - 2\,\Sigma\,(\phi^\dagger\gamma^\mu\psi)\,(\psi^\dagger\hat{\gamma}^\mu\phi)$$
$$-\,4\,(\phi^\dagger\gamma^5\psi)\,(\psi^\dagger\gamma^\mu\phi) \qquad (16, a)$$

$$4\,\Sigma\,(\psi^\dagger\gamma^\mu\psi)\,(\phi^\dagger\gamma^\mu\phi) = -\,4\,\Omega_1\Omega_1' + 2\,\Sigma\,\mathsf{S}_\mu\mathsf{S}_\mu' - 2\,\Sigma\,\hat{\mathsf{S}}_\mu\hat{\mathsf{S}}_\mu' - 4\,\Omega_2\Omega_2' \quad (16, b)$$

Both these lead to

$$3\,\Sigma\,\hat{\mathsf{S}}_\mu^2 - \Sigma\,\mathsf{S}_\mu^2 = -\,2\,\Omega_1^2 - 2\,\Omega_2^2 \qquad (16, c)$$

(6) $\mathbf{T} = \Sigma\,\gamma^{[\mu\nu]}\psi\phi^\dagger\gamma^{[\mu\nu]}$ or $\mathbf{T} = \Sigma\,\hat{\gamma}^{[\mu\nu]}\psi\phi^\dagger\gamma^{[\mu\nu]}$ and with $\phi\phi^\dagger$ [using the sixth row of (11)]:

$$-\,4\,\Sigma\,\mathsf{M}_{[\mu\nu]}\mathsf{M}_{[\mu\nu]}' = -\,4\,\Sigma\,\hat{\mathsf{M}}_{[\mu\nu]}\,\hat{\mathsf{M}}_{[\mu\nu]}'$$
$$= 6\,(\phi^\dagger\psi)\,(\phi^\dagger\phi) - 2\,\Sigma\,(\phi^\dagger\gamma^{[\mu\nu]}\psi)\,(\psi^\dagger\gamma^{[\mu\nu]}\phi)$$
$$+ 6\,(\phi^\dagger\gamma^5\psi)\,(\psi^\dagger\gamma^5\phi) \qquad (17, a)$$

$$4 \, \Sigma \, (\psi^\dagger \gamma^{[\mu\nu]} \phi) + 4 \, \Sigma \, (\phi^\dagger \gamma^{[\mu\nu]} \psi) = 4 \, \Sigma \, (\psi^\dagger \gamma^{[\mu\nu]} \phi) \, (\phi^\dagger \hat{\gamma}^{[\mu\nu]} \psi)$$
$$= - \, 6 \, \Omega_1 \Omega_1' + 2 \, \Sigma \, \mathbf{M}_{[\mu\nu]} \, \mathbf{M}'_{[\mu\nu]} + 6 \, \Omega_2 \Omega_2' \quad (17, b)$$

Both these lead to

$$\Sigma \, \mathbf{M}^2_{[\mu\nu]} = \Omega^2_1 - \Omega^2_2 \qquad (5, b) \text{ or } (17, c)$$

(7) $\mathbf{T} = \Sigma \, \gamma^{[\mu\nu]} \phi \phi^\dagger \gamma^{[\mu\nu]}$ or $\mathbf{T} = \Sigma \, \gamma^{[\mu\nu]} \psi \phi_1 \gamma^{[\mu\nu]} \phi$; and with $\phi \phi^\dagger$; [using the seventh row of (11)]:

$$- 4 \, \Sigma \, \mathbf{M}_{[\mu\nu]} \, \hat{\mathbf{M}}'_{[\mu\nu]} = - 4 \, \Sigma \, \hat{\mathbf{M}}_{[\mu\nu]} \, \mathbf{M}'_{[\mu\nu]}$$
$$= - \, 6 \, (\phi^\dagger \gamma^5 \psi) \, (\psi^\dagger \phi) - 2 \, \Sigma \, (\phi^\dagger \gamma^{[\mu\nu]} \psi) \, (\psi^\dagger \gamma^{[\mu\nu]} \phi)$$
$$- 6 \, (\phi^\dagger \psi) \, (\psi^\dagger \gamma^5 \phi) \qquad (18, a)$$

$$4 \, \Sigma \, (\psi^\dagger \gamma^{[\mu\nu]} \phi) \, (\phi^\dagger \hat{\gamma}^{[\mu\nu]} \psi) = 4 \, \Sigma \, (\psi^\dagger \gamma^{[\mu\nu]} \phi) \, (\phi^\dagger \gamma^{[\mu\nu]} \psi)$$
$$= 6i \, \Omega_1 \Omega_2' + 2 \, \Sigma \, \mathbf{M}_{[\mu\nu]} \, \hat{\mathbf{M}}'_{[\mu\nu]} + 6i \, \Omega_1 \Omega_2' \quad (18, b)$$

Both these lead to

$$\frac{1}{2} \, \Sigma \, \mathbf{M}_{[\mu\nu]} \, \hat{\mathbf{M}}_{[\mu\nu]} = \Omega_1 \Omega_2 \qquad (5, d) \text{ or } (18, c)$$

(8) $\mathbf{T} = \gamma^5 \psi \phi^\dagger \gamma^5$, $\mathbf{T} = \gamma^5 \phi \phi^\dagger \gamma^5$, [using the eighth row of (11)]
$$4 \, \Omega_2 \Omega_2' = (\phi^\dagger \psi) \, (\psi^\dagger \phi) - \Sigma (\phi^\dagger \gamma^\mu \psi) \, (\psi^\dagger \gamma^\mu \phi) + \Sigma \, (\phi^\dagger \gamma^{[\mu\nu]} \psi) \, (\psi^\dagger \gamma^{[\mu\nu]} \phi)$$
$$- \Sigma \, (\phi^\dagger \gamma^{\mu 5}) \, (\psi^\dagger \gamma^{\mu 5} \phi) + (\phi^\dagger \gamma^5 \psi) \, (\psi^\dagger \gamma^5 \phi) \qquad (19, a)$$

$$4 \, (\psi^\dagger \gamma^5 \phi) \, (\phi^\dagger \gamma^5 \psi) = - \, \Omega_1 \Omega_1' - \Sigma \, \mathbf{S}^2_\mu \mathbf{S}_\mu' - \Sigma \, \mathbf{M}_{[\mu\nu]} \, \mathbf{M}'_{[\mu\nu]}$$
$$- \Sigma \, \hat{\mathbf{S}}_\mu \hat{\mathbf{S}}_\mu' + \Omega_2 \Omega_2' \qquad (19, b)$$

Both these lead to

$$3 \, \Omega^2_1 + \Omega^2_2 = \Sigma \, \mathbf{S}^2_\mu - \Sigma \, \mathbf{M}^2_{[\mu\nu]} - \Sigma \, \hat{\mathbf{S}}^2_\mu \qquad (19, c)$$

Of these identities (14, c) or (15, c) give the identity (5, e); (17, c) is (5, b); (18, c) is (5, d). Also by addition and subtraction (13, c) & (16, c) give

$$\Sigma \, \mathbf{S}^2_\mu - \Sigma \, \hat{\mathbf{S}}^2_\mu = \Omega^2_1 - \Omega^2_2,$$

which proves (5, a) and (5, c). Thus all the identities (5) are proved without using Pauli's B-matrix All the generalised identities given by Pauli can be obtained as suitable linear combinations of our identities (12) to (19)

Thus (12, b) is the same as [P (39)]. {(12, b) + (19, b) or {2 (17, a) − (17, b)} gives

$$- \Omega_1 \Omega'_1 + \Omega_2 \Omega_2' - \Sigma \, \mathbf{M}_{[\mu\nu]} \, \mathbf{M}'_{[\mu\nu]} = 2 \, \{ (\phi^\dagger \psi) \, (\psi^\dagger \phi) + (\phi^\dagger \gamma^5 \psi) \, (\psi^\dagger \gamma^5 \phi) \}$$

which is [P. (43)].

$\{(12, b) - (19, b)\}$ or $\{(13, a) + (16, a)\}$ gives

$$\Sigma \, \mathbf{S}_\mu \mathbf{S}_\mu' + \Sigma \, \hat{\mathbf{S}}_\mu \hat{\mathbf{S}}_\mu' = 2 \, \{ (\phi^\dagger \psi) \, (\psi^\dagger \phi) - (\phi^\dagger \gamma^5 \psi) \, (\psi^\dagger \gamma^5 \phi) \}$$

which is [P, (44)].

$$\{(18,\,a) - 2\,(18,\,b)\}\ \text{gives}$$

$$i\,\Omega_1\Omega_2{}' + i\,\Omega_2\Omega_1{}' + \Sigma\,\hat{M}_{[\mu\nu]}\,M'_{[\mu\nu]} = 2\,\{(\phi^\dagger\psi)\,(\psi^\dagger\gamma^5) + (\psi^\dagger\phi)\,(\phi^\dagger\gamma^5\psi)\}$$

which is [P, (47)].

Finally $\{(14,\,a) - (15,\,a)\}$ gives

$$i\,\Sigma\,\hat{S}_\mu S_\mu{}' - i\,\Sigma\,\hat{S}_\mu S_\mu{}' = 2\,\{(\phi^\dagger\psi)\,(\psi^\dagger\gamma^5\phi) - (\psi^\dagger\phi)\,(\phi^\dagger\gamma^5\psi)\}$$

which is [P, (48)].

While these identities of Pauli are generalisations of $(5,\,b)$; $\{(5,\,a) + (5,\,c)\}$ and $(5,\,d)$ respectively, our identities contain generalisations of all the five in (5), as can be easily shown by taking suitable linear combinations. Similarly all the identities given by Harish-Chandra (pp. 35–36), in particular, his equations (32)–(36) are also linear combinations of our identities.

We note below a few other interesting identities :

$[(13,\,b) + (16,\,b)]$ gives

$$\Sigma\,(\psi^\dagger\gamma^\mu\psi)\,(\phi^\dagger\gamma^\mu\psi) + \Sigma\,(\psi^\dagger\hat{\gamma}\psi)\,(\phi^\dagger\hat{\gamma}^\mu\psi) = -\,2\,(\Omega_1\Omega_1{}' + \Omega_2\Omega'_2)$$

while $[(13,\,b) - (16,\,b)]$ or $[(13,\,a) - (16,\,a)]$ gives

$$\Sigma\,(\psi^\dagger\gamma^\mu\psi)\,(\phi^\dagger\gamma^\mu\psi) - \Sigma\,(\psi^\dagger\hat{\gamma}\psi)\,(\phi^\dagger\hat{\gamma}^\mu\psi) = -\,\Sigma\,S_\mu S_\mu{}' + \Sigma\,\hat{S}_\mu\hat{S}_\alpha{}' \quad (20,\,b)$$

Similarly $[(14,\,a) + (15,\,a)]$ or $[(14,\,b) + 15,\,b)]$ gives

$$\Sigma\,(\psi^\dagger\gamma^\mu\phi)\,(\phi^\dagger\gamma^\mu\psi) + \Sigma\,(\psi^\dagger\hat{\gamma}^\mu\phi)\,(\phi^\dagger\gamma^\mu\psi) = -\,\Sigma\,S_\mu\hat{S}_\mu{}' - \Sigma\,\hat{S}_\mu S_\mu{}' \quad (20,\,c)$$

and $[(14,\,b) - (15,\,b)]$ gives

$$\Sigma\,(\psi^\dagger\gamma^\mu\phi)\,(\phi^\dagger\gamma^\mu\psi) - \Sigma\,(\psi^\dagger\hat{\gamma}^\mu\phi)\,(\phi^\dagger\hat{\gamma}^\mu\psi) = 2\,(\Omega_1\Omega_2{}' - \Omega_2\Omega_1{}') \quad (20,\,d)$$

4   Tensor Identities

The bilinear and quadratic identities derived in the previous article lead to the invariant identities (5) and the corresponding expressions for T which give them might be considered magnitudes of 'invariant' type. It can be shown that by choosing other 'tensor' types for T we can deduce 'tensor' identities which might also involve a single pair $(\psi,\,\psi^\dagger)$ or two pairs $(\psi,\,\psi^1)$ and $(\phi,\,\phi^\dagger)$ We consider here identities of the first kind

Thus, for example, the 'vector' magnitude

$$T = \gamma^\mu\psi\psi^\dagger \qquad (21,\,a)$$

leads to the identity

$$4\,(\psi^\dagger\gamma^\mu\psi)\,(\psi^\dagger\psi) = \Sigma\,(\psi^\dagger\gamma^\nu\gamma^\mu\psi)\,(\psi^\dagger\gamma^\nu\psi)$$

and noting that

$$\gamma^\mu = -i\gamma^{[\mu\nu]}\gamma^\nu = \hat{i\gamma}^\nu\hat{\gamma}^{[\mu\nu]} \qquad (\mu \neq \nu)$$

and $\quad \hat{\gamma}^\mu = -i\gamma^\nu\gamma^\mu = i\hat{\gamma}^\mu\gamma^\nu$ $\Big\}$ **(1′)**

the right hand side reduces to

$$2\,(\psi^\dagger\gamma^\mu\psi)\,(\psi^\dagger\psi) - 2\sum_\nu (\psi^\dagger\hat{\gamma}^{[\mu\nu]}\psi)\,(\psi^\dagger\gamma^\nu\psi)$$

and we get

$$\Omega_1 S_\mu = \sum_\nu \hat{M}_{[\mu\nu]}\,\hat{S_\nu} \qquad (22)$$

which is H-C (37, a) *

Similarly

$$T = \sum_\nu \hat{\gamma}^\nu\psi\psi^\dagger\hat{\gamma}^{[\mu\nu]} \qquad (21, b)$$

also leads to the same identity

$$T = \hat{\gamma}^\mu\psi\psi^\dagger \ \text{or} \ T = \sum_\nu \gamma^\nu\psi\psi^\dagger\hat{\gamma}^{[\mu\nu]} \qquad (21, c)$$

leads to

$$\Omega_1\hat{S}_\mu = -\sum_\nu \hat{M}_{[\mu\nu]}\,S_\nu \qquad (23)$$

which is H-C (37, b)

Either of the magnitudes

$$T = \hat{\gamma}^\mu\psi\psi^\dagger\gamma^5 \ \text{or} \ T = \sum_\nu \gamma^\nu\psi\psi^\dagger\gamma^{[\mu\nu]} \qquad (21, d)$$

gives Bhabha's identity [H-C (37, d)]

$$i\,\Omega_2\hat{S}_\mu = -\sum_\nu M_{[\mu\nu]}S_\nu. \qquad (24)$$

Similarly,

$$T = \gamma^\mu\psi\psi^\dagger\gamma^5 \ \text{or} \ T = \sum_\nu \hat{\gamma}^\nu\psi\psi^\dagger\gamma^{[\mu\nu]} \qquad (21, e)$$

gives

$$i\,\Omega_2 S_\mu = \sum_\nu M_{[\mu\nu]}\,\hat{S_\nu} \qquad (25)$$

which is H-C (37, e)

The above magnitudes are of vector type. We can consider, further, those of a tensor type of the second order. Thus for example each of the following four expressions

$$T = \gamma^{[\mu\nu]}\psi\psi^\dagger; \ \gamma^{[\mu\nu]}\psi\psi^\dagger\gamma^5; \ \gamma^\mu\psi\psi^\dagger\hat{\gamma}^\nu; \ \hat{\gamma}^\mu\psi\psi^\dagger\gamma^\nu \ (\mu \neq \nu) \qquad (21, f)$$

gives rise to

$$S_\mu \hat{S} - S_\nu \hat{S}_\mu = \imath \, \Omega_2 \, M_{[\mu\nu]} - \Omega_1 \, \hat{M}_{[\mu\nu]} \qquad (26)$$

which is H-C (37, c)

Similarly

$$T = \gamma^\mu \psi \psi^\dagger \gamma^\nu \quad \text{or} \quad T = \hat{\gamma}^\mu \psi \psi^\dagger \hat{\gamma}^\nu \qquad (21, g)$$

gives

$$S_\mu S_\nu + \hat{S}_\mu \hat{S}_\nu = \sum_\rho M_{[\mu\rho]} \, M_{[\nu\rho]} \qquad \text{(for } \mu \neq \nu) \qquad (27, a)$$

and

$$S_\mu^2 + \hat{S}_\mu^2 = \sum_\rho M_{[\mu\rho]}^2 - \Omega_1^2 \qquad \text{(for } \mu = \nu) \qquad (27, b)$$

Both (27, a) and (27, b) are included in H-C (37, f).

Equation (26) is identically satisfied for $\mu = \nu$, but it can be shown that by taking

$$T = \gamma^\mu \psi \psi^\dagger \hat{\gamma}^\mu \qquad (21, h)$$

we get immediately the quadratic identity (5, e). viz., $\sum S_\mu \hat{S}_\mu = 0$ which was deduced in (14, c) by taking for T the expression (21, h) summed over μ. In a similar manner, we observe that by taking

$$T = \gamma^{[\mu\nu]} \psi \psi^\dagger \hat{\gamma}^{[\mu\nu]} \qquad (21, i)$$

we are led to (5, d) without the summation over $[\mu\nu]$ as in (16, i).

Finally the 'pseudo-scalar' magnitude

$$T = \gamma^5 \psi \psi^\dagger$$

can be shown to lead to (5, d) directly just as (21, i)   (21, j)

We also notice that the quadratic invariant identities can be deduced from the above tensor identities (22)–(27). Multiplying both sides of (22) by $\hat{S}_\mu$ and summing over μ, the right-hand side which becomes a double summation over μ and ν reduces to zero in view of the anti-symmetry of $\hat{M}_{[\mu\nu]}$ and hence $\sum S_\mu \hat{S}_\mu = 0$, which is (5, e)   This also results by applying a similar procedure to (23), (24) or (25). Next multiplying both sides of (26) by S_μ, and summing over μ we get, using (23), (24) and (5, e) deduced above, that

$$\sum S_\mu^2 = -\Omega_1^2 - \Omega_2^2$$

which is (5, a). Multiplying both sides of (22) by S_μ, summing over μ, and using (23) we derive

$$\sum S_\mu^2 = \sum \hat{S}_\mu^2$$

and each equal to $-\Omega_1^2 - \Omega_2^2$ which is (5, c). Substituting these values in (27, b) gives immediately

$$\Sigma \, \mathbf{M}^2_{[\mu\nu]} = \Omega_1^2 - \Omega_2^2$$

which is (5, b). Finally to obtain (5, d) we multiply (25) by $\mathbf{M}_{[\mu\nu]}$ and sum over μ and ν. This gives, using (22) and (23),

$$2 \, \Omega_2 \, \underset{[\mu\nu]}{\Sigma} \, \mathbf{M}^2_{[\mu\nu]} + 2 \, i \, \Omega_1 \, \underset{[\mu\nu]}{\Sigma} \, \mathbf{M}_{[\mu\nu]} \, \hat{\mathbf{M}}_{[\mu\nu]} = 2 \, \Omega_2 \, \underset{\mu}{\Sigma} \, (\mathbf{S}_{\mu}^2 + \hat{\mathbf{S}}_{\mu}^2) \qquad (28)$$

Substituting from (5, a, b, c) this leads to

$$-\frac{i}{2} \, \Sigma \, \mathbf{M}_{[\mu\nu]} \, \hat{\mathbf{M}}_{[\mu\nu]} = \Omega_1 \, \Omega_2$$

which is (5, d).

The above derivation further enables us to show that the six tensor identities (22) to (27) are not all independent. In fact, (27) can be deduced from the remaining ones. Thus, multiplying (26) by $\mathbf{M}_{[\nu\rho]}$ on both sides and summing over ν, we get

$$\underset{\nu}{\Sigma} \, \Omega_2 \, \mathbf{M}_{[\mu\nu]} \, \mathbf{M}_{[\nu\rho]} + i \, \Omega_1 \, \underset{\nu}{\Sigma} \, \hat{\mathbf{M}}_{[\mu\nu]} \, \mathbf{M}_{[\nu\rho]} + \Omega_2 \, (\mathbf{S}_{\mu} \mathbf{S}_{\rho} + \hat{\mathbf{S}}_{\mu} \hat{\mathbf{S}}_{\rho}) = 0,$$

in virtue of (24) and (25). The second summation of the left is easily seen to be identically equal to zero, and we have (27, a), i.e., ($\mu \neq \rho$). To derive (27, b), we multiply (24) and (25) by $\hat{\mathbf{S}}_{\mu}$ and $\mathbf{S}_{\mu}$ respectively, add and use (25) which yields

$$\Omega_2 \, (\mathbf{S}_{\mu}^2 + \hat{\mathbf{S}}_{\mu}^2) = \underset{\nu}{\Sigma} \, \Omega_2 \, \mathbf{M}^2_{[\mu\nu]} + i \, \underset{\nu}{\Sigma} \, \Omega_1 \, \mathbf{M}_{[\mu\nu]} \, \hat{\mathbf{M}}_{[\mu\nu]} \qquad (29, a)$$

Similarly (22) and (23) give

$$\Omega_1 \, (\mathbf{S}_{\mu}^2 + \hat{\mathbf{S}}_{\mu}^2) = \underset{\nu}{\Sigma} \, \hat{\mathbf{M}}^2_{[\mu\nu]} + i \, \underset{\nu}{\Sigma} \, \Omega_2 \, \mathbf{M}_{[\mu\nu]} \, \hat{\mathbf{M}}_{[\mu\nu]} \qquad (29, b)$$

Equation (29, a) and (29, b)

$$i \, (\Omega_1^2 - \Omega_2^2) \, \underset{\nu}{\Sigma} \, \mathbf{M}_{[\mu\nu]} \, \hat{\mathbf{M}}_{[\mu\nu]} = -\Omega_1 \, \Omega_2 \, \{\underset{\nu}{\Sigma} \, (\mathbf{M}^2_{[\mu\nu]} + \hat{\mathbf{M}}^2_{[\mu\nu]})\}$$
$$= -\Omega_1 \, \Omega_2 \, \underset{[\mu\nu]}{\Sigma} \, \mathbf{M}^2_{[\mu\nu]}$$

This along with (28) above determines $\underset{\nu}{\Sigma} \, \mathbf{M}_{[\mu\nu]} \, \hat{\mathbf{M}}_{[\mu\nu]}$ which, when substituted in (29, a) gives (27, b). Thus we have shown that (27, a, b) can be deduced from (22)–(26), or there are only five independent tensor identities.

5. Multilinear, and Polynomial Identities

The matrices T used in the derivation of the quadratic identities are of the form $\gamma^{\Lambda} \phi \phi^{\dagger}$, and to derive higher polynomial identities, one has only to take T as the product of two or more such types of expressions. The

procedure mentioned in §2 then shows that the identities thus obtained are merely certain multiples of the quadratic identities. For example,

$$T = \gamma^A \psi \phi^\dagger \gamma^B \psi \phi^\dagger$$

gives the cubic identity

$$4 \; (\psi^\dagger \gamma^A \psi) \; (\psi^\dagger \gamma^B \psi) \; (\phi^\dagger \psi) - \sum_C (\psi^\dagger \gamma^C \gamma^A \psi) \; (\psi \gamma^B \psi) \; (\psi \gamma^C \psi)$$

and this can be obtained, by multiplication with $(\phi^\dagger \gamma^B \psi)$, from the quadratic identity

$$4 \; (\phi^\dagger \gamma^A \psi) \; (\psi^\dagger \psi) = \sum_C (\psi^\dagger \gamma^C \gamma^A \psi) \; (\phi^\dagger \gamma^C \psi)$$

derivable with the aid of $T = \gamma^A \psi \phi^\dagger$. Thus polynomial identities are derivable from quadratic ones. Similarly multilinear identities can be derived from bilinear ones. To illustrate this we consider a slightly complicated example by taking

$$T = \sum_\mu \; (\gamma^\mu \phi \phi^\dagger \gamma^\mu \psi \psi \phi^\dagger \gamma^\mu) \tag{30}$$

and use $\chi^\dagger$ and χ for multiplication on the left and right. (30) yields the trilinear identity

$$4 \sum_\mu (\chi^\dagger \gamma^\mu \phi) \; (\psi^\dagger \gamma^\mu \psi) \; (\phi^\dagger \gamma^\mu \chi) = \sum_\lambda \sum_\mu (\phi^\dagger \gamma^\mu \gamma^\lambda \gamma^\mu \phi) \; (\psi^\dagger \gamma^\mu \psi) \; (\chi^\dagger \gamma^\lambda \chi) \tag{31}$$

The corresponding bilinear identity would be given by

$$T = \sum_\mu \gamma^\mu \phi \phi^\dagger \gamma^\mu \tag{30, a}$$

which on multiplication by $\chi^\dagger$ on the left, and χ on the right yields

$$4 \sum_\mu (\chi^\dagger \gamma^\mu \phi) \; (\phi^\dagger \gamma^\mu \chi) = \sum_\lambda \sum_\mu (\phi^\dagger \gamma^\mu \gamma^\lambda \gamma^\mu \phi) \; (\chi^\dagger \chi^\lambda \gamma) \tag{31, a}$$

which is also (13, b). On account of the summation over μ, the trilinear identity (31) is not given directly as a mere multiple of (31,) with $S_\mu = (\psi^\dagger \gamma^\mu \psi)$ as the factor. But it would still be possible to derive (31) by mere multiplication from a different kind of bilinear identity, viz., a tensor one Thus we could take

$$T = \gamma^\mu \phi \phi^\dagger \gamma^\mu \qquad \text{(no summation)} \tag{30, b}$$

and derive the 'tensor' bilinear identity

$$4 \; (\chi^\dagger \gamma^\mu \phi) \; (\phi^\dagger \gamma^\mu \chi) = \sum_\lambda \; (\phi^\dagger \gamma^\mu \gamma^\lambda \gamma^\mu \phi) \; (\chi^\dagger \gamma^\lambda \chi) \tag{31, b}$$

which is the generalization of the quadratic tensor identity (27, b). Multiplying both sides of (31, b) by $\psi^\dagger \gamma^\mu \psi$ and summing over μ, we go over to (31). The same situation presents itself when considering the cubic identity obtained from (31) by putting $\psi = \phi = \chi$ and $\psi^\dagger = \phi^\dagger = \chi^\dagger$ viz

$$\sum S_\mu^\natural + \sum S_\mu \hat{S}_\mu^\natural + \Omega_1^2 \sum S_\mu = \sum \sum S_\mu \, M_{[\mu\nu]}^\natural \tag{32, a}$$

and the analogous one obtained by taking the dual of γ^μ in (30),

$$\Sigma \; \hat{S}^a_\mu + \Sigma \; \hat{S}'_\mu S^2_\mu + \Omega_2 \; \hat{S}_\mu = \Sigma \; \hat{S}_\mu \; M^2_{[\mu\nu]} \qquad (32,\,b)$$

(32, a) and (32, b) are not simple multiples of the associated quadratic invariant identity (12, c) or (19, c), viz.

$$\left.\begin{array}{l} \Sigma \; S^3_\mu + \Sigma \; \hat{S}^3_\mu + 3\Omega^2_1 + \Omega^2_2 = \displaystyle\sum_{[\mu\nu]} M^3_{[\mu\nu]} \\[2mm] \Sigma \; S^3_\mu + \Sigma \; \hat{S}'_\mu + 3\Omega^2_2 + \Omega^2_1 = \displaystyle\sum_{[\nu\mu]} M^3_{[\mu\nu]} \end{array}\right\}$$

or

but can be obtained from the tensor identity (27, b), i.e.

$$S^2_\mu + \hat{S}^2_\mu + \Omega^2_n = \sum_\nu M^2_{[\mu\nu]}$$

by multiplying with S_μ or $\hat{S}_\mu$ and summing over μ

6. Primitive Types of Matrices

We will now show that all the identities considered in this paper can be deduced by considering the five primitive types of matrices

$$T = \psi\psi^\dagger, \; \gamma^\mu\psi\psi^\dagger, \; \gamma^{[\mu\nu]}\psi\psi^\dagger, \; \hat{\gamma}^\mu\psi\psi^\dagger, \; \gamma^5\psi\psi^\dagger \qquad (2,\,a)$$

given as the product of the five types of γ^A and matrices of rank unity. Since polynomial and multilinear identities are deducible from quadratic and bilinear ones respectively, we confine ourselves to the latter kinds. Let us consider the quadratic case where only one pair $(\psi,\,\psi^\dagger)$ appears;

$T = \psi\psi^\dagger$ gives the invariant identity

$$\Sigma \; S^2_\mu + \Sigma \; \hat{S}'_\mu - \sum_{[\mu\nu]} M^2_{[\mu\nu]} = -3 \; \Omega^2_1 - \Omega^2_2 \qquad (12,\,c)$$

$T = \gamma^\mu\psi\psi^\dagger$ gives the tensor identity

$$\sum_\nu \hat{M}_{[\mu\nu]} \; \hat{S}_\nu = \Omega_1 \; S_\mu \qquad (22)$$

$T = \gamma^{[\mu\nu]}\psi\psi^\dagger$ gives the tensor identity

$$\Omega_2 \; M_{[\mu\nu]} + i \; \Omega_1 \; \hat{M}_{[\mu\nu]} + i \; (S_\mu\hat{S}_\nu - S_\nu\hat{S}_\mu) = 0 \qquad (26)$$

$T = \hat{\gamma}^\mu\psi\psi^\dagger$ gives the tensor identity

$$\sum_\nu \hat{M}_{[\mu\nu]} = -\Omega_1 \; \hat{S}_\mu \qquad (23)$$

and $T = \gamma^5\psi\psi^\dagger$ gives the invariant identity $-\dfrac{i}{2}\displaystyle\sum_{[\mu\nu]} M_{[\mu\nu]} \; \hat{M}_{[\mu\nu]} = \Omega_1\Omega_2 \quad (5,\,d)$

As shown in §4, (22) and (23) give $\Sigma \; S^2_\mu = \Sigma \; \hat{S}^2_\mu$, and (22) or (23) gives $\Sigma \; S_\mu\hat{S}_\mu = 0$. Multiplying (26) by $M_{[\mu\nu]}$, using (22) and (23), and summing

over μ and ν, and also taking (5, d) into account we get a relation between $\Sigma\,S_\mu^2$ and $\Sigma\,M_{[\mu\nu]}^2$ other than (12, c). Taking (12, c) into consideration therefore gives

$$\Sigma\,S_\mu^i\quad \Sigma\,\hat{S}_\mu^i = -\,\Omega_1^2 + \Omega_2^2; \ \ \Sigma\,M_{[\mu\nu]}^2 = \Omega_1^2 - \Omega_2^2$$

and all the invariant quadratic identities are thus derived.

We have next to obtain the tensor identities (24) and (25) since the remaining one, $viz.,$ (27) has previously been shown to be a consequence of the others. This is easily done by means of (26). Multiplying it by S_ν and summing over ν we get, using (23) and (5 e)

$$\Omega_2\,\Sigma\,M_{[\mu\nu]}\,S_\nu + \iota\,\Omega_1\,(-\,\Omega_1\,\hat{S}_\mu) = \iota\,\hat{S}_\mu\,\Sigma\,S_\nu^2$$

and since $\Sigma\,S_\nu^2 = -\,\Omega_1^2 - \Omega_2^2$, this gives

$$\Sigma\,M_{[\mu\nu]}\,S_\nu = \iota\,\Omega_2\,\hat{S}_\mu$$

which is (24). Similarly multiplication by $\hat{S}_\nu$ in (26) leads to (25). Hence (33) yield all the quadratic invariant and tensor identities.

The proof that (33) also lead to the bilinear identities of the invariant and tensor forms can be carried out in a similar, though much more complicated manner, and need not be explicitly given here. We will notice, however, only one simple case. The last matrix in (33), $T = \gamma^\lambda\psi\phi^\dagger$ gives the bilinear identity

$$\begin{aligned}
4\,(\phi^\dagger\gamma^\lambda\psi)\,(\psi^\dagger\phi) &= \Sigma\,(\psi^\dagger\gamma^\lambda\psi)\,(\phi^\dagger\gamma^\lambda\phi) \\
&= \iota\,\Omega_1\Omega_2' + \iota\,\Omega_2\Omega_1' - \iota\,\Sigma\,\hat{S}_\mu S_\mu' + \iota\,\Sigma\,S_\mu\hat{S}_\mu' \\
&\qquad\qquad - \Sigma\,\hat{M}_{[\mu\nu]}\,M_{[\mu\nu]}' \quad (34)
\end{aligned}$$

Interchanging ϕ and ψ interchanges the dashed and undashed quantities on the right of (34). Adding and subtracting (34) and the expression thus obtained we get immediately (P 47) and (48).

SUMMARY

It is shown in this paper that by choosing suitable forms for 4×4 matrices as products of Dirac matrices and matrices of rank unity ($i.e$, products of 4×1 and 1×4 matrices), and expressing them as linear combinations of the sixteen elements γ^λ of the basis of the Dirac algebra, one can derive the generalized identities of Pauli which hold in this algebra. Generalizations are given for cases not dealt with by Pauli, and the use of his B-matrix is also avoided. The same method yields further 'tensor', multilinear, and polynomial identities of which it is shown that the last two

kinds of identities are derivable from bilinear and quadratic ones. It is
pointed out that all types of identities can be deduced by considering five
primitive types of matrices.

REFERENCES

Harish-Chandra	Proc. Ind Acad. Sci., 1945, **22**, 30.
D. E. Littlewood	J. L. M S., 1934, 9, 41
W. Pauli	Annales de l'Institut H Poincare, 1936, 109.

INDEX TO VOL. XXII (A)

AUTHORS' INDEX

TITLE INDEX